SYMPOSIUM ON CHEMICAL PROCESS HAZARDS WITH SPECIAL REFERENCE TO PLANT DESIGN.

MANCHESTER 1960

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1. Chemical accidents
2. hazardous Processes
3. instrumentation
4. pentane vapour air explosions
5. ethylene oxide vapour
6. explosion hazards
7. flame explosions.
9. industrial drying ovens
10. hydrofluoric acid

The Institution of Chemical Engineers
North-Western Branch

PROCEEDINGS OF THE

SYMPOSIUM ON CHEMICAL PROCESS HAZARDS WITH SPECIAL REFERENCE TO PLANT DESIGN

MANCHESTER 29–31 MARCH, 1960

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PAPERS AND DISCUSSION AT THE FIRST SESSION

SOME SIGNIFICANT CHEMICAL ACCIDENTS

By DONALD MATHESON, M.A., B.Sc., Ph.D.*

SUMMARY

In deciding the precautions that should be taken to prevent accidents that may arise from causes of a chemical nature, certain simple principles are followed. Judgment must be exercised, however, in the apportioning of emphasis in the application of the principles. It is by the study and the investigation of accidents that one discovers the conditions that are most frequently associated with them and the conditions that give rise to the greatest disasters. This paper contains a description of some accidents that are typical of those that have led particular importance to be attached to certain precautions.

Introduction

For more than twenty years chemists in the Factory Inspectorate have followed a clearly formulated set of principles in determining the precautions that should be taken to prevent accidents that may arise from causes of a chemical nature. These principles are derived from the elementary, self-evident principle that, if a person is liable to suffer injury by contact with a dangerous substance, precautions should be taken to prevent the contact. In the present context contact may be direct or indirect. Injury from direct contact may occur, for example, when a man is splashed by corrosive material, in which case the contact is external, or when he breathes a poisonous gas or vapour, in which case the contact is internal. A dangerous substance may cause injury in another way when it burns or explodes. In this case the contact with the dangerous material is indirect.

The most effective way of ensuring that a person will not be injured by direct contact with a dangerous substance is to replace the dangerous substance by a safe one which is also capable of serving the purpose of the process. Alumina is used as a safe and effective substitute for silica in pottery saggars ; and steam or hot water (sometimes in conjunction with a wetting agent) can often be used instead of benzene for oil and fat extraction, thus avoiding the well-known danger associated with the inhalation of benzene vapour. Even when there is no completely safe material that can be used for the purpose served by the dangerous material, a considerable step towards safety is often taken by the substitution of a less dangerous one : trichlorethylene or white spirit are used nowadays for many purposes for which carbon tetrachloride or benzene were used in the past.

In many instances, however, a dangerous substance must still be used, and, in such a case, the principle that is followed in the prevention of contact is that of imposing a barrier between the dangerous substance and the persons who would otherwise be exposed to the danger. Fencing is provided round acid tanks, and lead shrouds are fitted round flanged joints in pipe-lines where leaks of corrosive liquids could take place. In processes from which poisonous gases, vapours, or dusts are liable to be evolved the barrier may take the form of complete enclosure of the plant with arrangements for operating the process from outside the enclosure. In such a case the enclosure may be under exhaust ventilation. A modern example of this type of enclosure is the glove-box so commonly used in the handling of radioactive materials. For the purposes of manipulation it is often necessary to provide an opening in the enclosing barrier. This opening should be no larger than is necessary for the operations that must be carried out, and the exhaust ventilation that is applied to the enclosure should ensure that the velocity of air passing through the opening from the workroom into the enclosure is such that there is no outward drift of toxic material into the air of the workroom. In other words the principle of the chemists' fume-cupboard in all shapes, forms, and sizes is followed. For purposes of maintenance it is often necessary that someone should enter a vessel that has contained a dangerous material. In such a case the vessel should be isolated and purged to remove gases and vapours with which the person entering would otherwise have contact. Sludge or scale should be washed out with a hose. After all this has been done the vessel should be tested for gas before entry. If sludge or scale cannot be removed before entry, the person entering should wear breathing apparatus and a life-line and a watcher should be stationed outside the vessel.

The principles governing the precautions to be taken in the case of substances that form flammable or explosive mixtures with air can be more briefly stated. When the process allows it, steps should be taken to avoid the presence of the flammable or explosive mixture. This may be done by the substitution of a non-flammable or a less flammable material, by the use of exhaust ventilation to remove flammable gases, vapours, or dusts, or by the use of inert gas. Sources of ignition should be eliminated as far as possible and precautions should be taken to minimise the spread and effects of a fire or explosion. In other words, a fire or explosion, commencing in a small way, should be prevented from becoming a large one, and an explosion, starting in some part of the plant where it would do comparatively little harm, should be prevented from spreading to a part where it could do injury and damage.

While the principles themselves can be described in a few minutes, the art of applying the principles is something that is learned over a life-time. It is by the study and the investigation of accidents that one discovers the conditions that are most frequently associated with them and the conditions that give rise to the greatest disasters. In this way a basis is established for the exercise of judgment in the apportioning of emphasis in the application of the principles. It has been proposed therefore that this paper should contain a description of some

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accidents that are typical of those that have led us to attach particular importance to certain precautions.

Gassing Accidents

Some of the worst gassing accidents have occurred to men who were working inside plant or other confined spaces. If a dangerous gas or vapour is liable to be present inside a confined space of this nature, the risk is obvious and stringent legal requirements indicate the precautions that are deemed to be necessary when work has to be done in such conditions. It is not the purpose of this paper to consider in detail the requirements of the Factories Acts, but it should be noted in connection with what follows that Section 27 of the Factories Act, 1937 as amended by Section 6 of the Factories Act, 1959 requires that, where work has to be done inside any chamber, tank, vat, pit, pipe, flue, or similar confined space, in which dangerous fumes are liable to be present to such an extent as to involve risk of persons being overcome thereby, the confined space shall not be certified as safe for entry without breathing apparatus unless, amongst other precautions, effective steps have been taken to prevent any ingress of dangerous fumes. In Regulation 7 of the Chemical Works Regulations it is required that such a place shall be certified as isolated and sealed from any source of dangerous gas or fume. The lesson that was learned from the accident described in the following paragraph was that, if isolation in such circumstances is to be effective, it must be well designed to conform with high standards.

Examples and their lessons

In a chemical factory a battery of four pans was being used for a process in which hydrogen sulphide was generated. Each pan was connected by a short duct to a common main fitted with an exhaust fan to draw fumes away from the pans. On each duct was a valve for the purpose of shutting off the pan from the main. On the day of the accident three of the pans were working and were open to the main. The fourth pan was standing idle awaiting some minor alteration. It had been steamed out and washed clean the previous day, the valve had been closed with the intention of isolating the pan from the main, and all other pipes to the pan were disconnected. After mice had been exposed inside the pan for an hour for the purpose of testing the atmosphere and had shown no signs of distress a man entered to carry out the alteration in question, but he was called away a few minutes later to another job. He entered again an hour later, without further test, and was at once overcome and killed by hydrogen sulphide. Two men, who attempted a rescue without breathing apparatus, were also overcome and one of them died.

After the accident it was found that the belt had come off the pulley of the exhaust fan. The valve was found to be closed as far as it would go, and evidence showed that it had not been opened accidentally : it was found, however, to leak slightly under a pressure of several inches of water. While the fan was working this defect in the valve did not result in the entry of gas into the pan and the test indicated safe conditions.

This accident is typical of many that illustrate the absolute necessity of completely disconnecting, and blanking off, from all possible sources of dangerous gas, any plant that is to be entered. No other precaution can take the place of disconnecting and blanking off. A spectacle valve, properly bolted with a made joint, is a form of disconnection and blanking. Incidentally, although reliance on the use of mice was not the cause of this accident, it should be appreciated that mice are not safe indicators except for carbon monoxide and hydrogen cyanide. Chemical tests should be used wherever, as in the case of hydrogen sulphide, reliable tests have been devised.

Even when a vessel has been thoroughly purged with steam and air and has been completely isolated from every possible source of dangerous fume, and the atmosphere inside it has been tested and shown to be safe, that vessel may still be unsafe to enter without breathing apparatus and a life-line. It may be unsafe to enter if it contains sludge. During the last war a process for the cleaning of tanks attracted the attention of people who had to concern themselves with this problem in marine and land transport and in factories like chemical works. The process depended upon the treatment of the tanks with carbon tetrachloride. Hot carbon tetrachloride vapour from a special portable boiler was injected into the closed tank. This dissolved the tarry deposits on the inside walls of the tank, and, after a suitable number of injections had been given, the solution of the tarry material in the condensed vapour was discharged through the cock at the bottom of the tank. A railway tank-wagon, that had been treated in this manner, was left with the top manhole and the bottom cock open for nine days. The atmosphere was tested at intervals and on the ninth day, when the test indicated that the atmosphere inside the tank was safe, a foreman entered. He could smell no vapour. The next day a workman entered and removed some of the tarry sludge that remained on the bottom of the tank. On that occasion he was unaffected. Two days later, the tank having remained open in the meantime, he entered again and continued the removal of the sludge. After he had been working for about an hour he was overcome by the fumes which no doubt were released from the sludge that he was disturbing.

This was not a fatal accident ; the man recovered. The story has not been introduced because of any disastrous element in it, but because it provides a good example of the unpredictable and insidious behaviour of sludge. Many fatal accidents have occurred, however, because of the presence of sludge and scale. In one instance acid was used to decompose sulphides in a process for the extraction of iodine from seaweed. Some of these sulphides were present in a crust that formed on the top of the liquor. Most of the liquor was discharged from the tank and, after ventilation for a number of days, the atmosphere inside it was tested and found to be safe. Two men then entered to clean out the residual sludge. In doing so they disturbed the crust containing the sulphides and caused it to come into more intimate contact with the remaining acid whereby hydrogen sulphide was liberated. Both men were killed and men standing outside in the vicinity of the tank opening were overcome. In another instance two men, who were cleaning scale from the inside of a petrol storage tank, died from the effects of lead tetraethyl in spite of the fact that the tank had been positively ventilated for months before entry, and the air inside it had been tested with great care.

Warned by such accidents, the factory inspector considers that the presence of sludge or scale calls for precautions, in the form of breathing apparatus and life-lines, that are no less thorough than those required in the case of the presence of the dangerous gas itself.

Explosions

During the past twenty years the attitude of people, who have had to concern themselves with the problem of explosions on industrial plant, has changed very considerably Previously the general tendency was to make an exhaustive

study of the possible sources of ignition—a most necessary undertaking—and to support precautions based on that study by a few additional precautions, which, although useful in themselves, did not play a part in any systematically planned general scheme. Nowadays increasing attention is being paid to the avoidance of flammable concentrations when the substance is capable of forming explosive mixtures with air, and to precautions aimed at limiting the spread and effects of an explosion. The next three accounts are typical examples of the severe education we received on the subject of dust explosions.

Examples and their lessons

In a provender factory cotton-seed cake was being ground in a mill in the basement of the building, and the ground material was being carried by a bucket elevator passing through several floors to the bins at the top of the building. The ground material was ignited by some means, perhaps by the friction set up by a bucket of the elevator that was later found to be loose inside the casing. A dust explosion took place inside the elevator and the casing was burst in a number of places. The investigation seemed to show that no one was injured by the primary explosion in the elevator. But there were accumulations of loose dust in the rooms through which the elevator passed, and the explosion in the elevator dislodged this loose dust, giving rise to dust-clouds in the workrooms. Flame from the burst elevator casing ignited the dust-clouds and a secondary dust explosion spread throughout the factory. The building was wrecked, six people were killed in the secondary explosion, and a large number of people was injured.

The lesson to be learnt from such explosions is the disastrous character of a secondary dust explosion in the workrooms and the vital necessity of avoiding the possibility of inflammable concentrations of dust in the workrooms. In other words, we have learned to appreciate the necessity for the exercise of scrupulous cleanliness to prevent the formation of accumulations of dangerous dust in the workrooms.

In a somewhat similar secondary explosion in a cork mill the explosion spread from one room to another and indeed, by communicating galleries and enclosed bridges, from one building to another. Five men of a reduced night staff were killed by this explosion.

The previous lesson was confirmed and additional evidence was provided of the need for effective separation of workrooms and buildings to limit the spread of the explosion.

The manufacture of fine metal powders, such as those of aluminium and magnesium, has been associated with many disastrous dust explosions. The following account of a magnesium dust explosion is not being given as an example of an explosion that had disastrous consequences: it has been included because the explosion in question played a considerable part in establishing the attitude that should be adopted concerning the precautions to recommend for the manufacture of aluminium and magnesium powders, and in confirming the views already adopted concerning dust-settling plant in general such as cyclones, bag-filters, and settling chambers. The plant that was associated with the explosion consisted of a hammer-mill with a coupled fan for the pneumatic conveyance of the ground material, a separator for over-size material, and three cyclones arranged in series in such a manner that the coarsest material was settled in the first, the medium-range material in the second, and the finest powder in the third. Originally the cyclones were installed inside the building, but, some time before the explosion occurred, the firm had transferred them to a small yard outside. During a meal interval, while the mill was running under the supervision of the only workman remaining on the premises, an explosion occurred on the plant which caused the complete disintegration of the third cyclone, wrecked the second, and considerably damaged the first. The workman was not near the cyclones at the time and he escaped with very minor injuries, but surrounding buildings were damaged. If at the time of the explosion the cyclones had still been inside the building and men had been working there an explosion of this violence would have been disastrous.

This explosion provided impressive evidence of the unusual violence that is associated with the explosions of certain metal powders and dusts. Subsequent explosions and experimental work confirmed this evidence. It was realized therefore that precautions for the manufacture of such powders would have to be particularly severe. In one or two instances successful arrangements were made to avoid flammable concentrations by the use of inert gas. But in the great majority of processes the possibility had to be accepted that an explosion could occur. To ensure that the people working in the factory would not be injured by the explosion, the plant on which an explosion could occur had to be housed in strong cubicles with explosion reliefs relieving to the open air. The doors giving access to the cubicles had to be strong doors interlocked with the drive in such a manner that the cubicle could not be entered while the plant was running. The process was controlled from outside the cubicle. Sometimes certain parts of the plant could be situated in the open air, in a safe place that could not be approached while the plant was running. In such a case the controls were usually operated on the safe side of a strong wall inside the factory.

The precaution of isolating dangerous plant from occupied workrooms has been applied to plant in which explosions other than those of metal powder are liable to occur. It is known that explosions in settling plant, like cyclones and bag-filters, can be particularly violent, and it has become a practice to urge that such plant be installed in the open air or be otherwise isolated from the workroom.

Experience has shown that bucket elevators inside a factory can be similarly dangerous, and they have the added danger, that, since they generally pass through a number of floors, they can start simultaneous, secondary explosions in a number of storeys of the building. It is good, safe practice to install them in a separate tower on an outside wall of the factory building or to replace them by safer types of elevators.

Fire and explosion

The danger of fire and explosion associated with flammable liquids and their vapours has been well appreciated and it has for long been customary to take certain precautions. For example, it has been the practice to provide bund walls round storage tanks to retain flammable liquid in the event of spillage and to prevent it from flowing to a place where it could become ignited and cause a serious fire in the storage area. Storerooms have been provided with raised sills at doorways to serve the same purpose. It has not been so readily recognized, however, that similar precautions are required for flammable liquids in actual use in the process. Sometimes the quantity of liquid present at any time in the process plant is as great as that present in a large store. It may be present at different levels in the building, and, in the absence of precautions, a serious leak may endanger the whole factory and the people in it. This observation is so obvious that no one would seek to deny its truth, yet it has been remarkably difficult at

times to convince those responsible for such plant that precautions were needed to prevent the spread of spilt liquid in process similar to those provided for liquid in storage. Indeed difficulty has been experienced in dissuading a company from using open chequer plate flooring in a multi-storey building in which large quantities of flammable liquids were used at different levels in the building.

The danger resulting from the spread of spilt flammable liquid from a process vessel is exemplified by an explosion that occurred in a factory in which flammable solvent was used in an extraction process. A tank containing extracted material in solution split at a seam and liquid poured out on to the floor of the room. There were no arrangements to prevent the liquid from spreading and it spread through doorways and through openings in the floors to lower levels of the factory. In the meantime the air of the workrooms was becoming charged with flammable vapour which was soon ignited. In the explosion that ensued twelve people were killed.

After this accident, opinions that were held concerning the necessity for kerbs and sills to restrict the spread of spilt liquid from process vessels became convictions. When new plant is being installed for processes using flammable liquids, the arrangement of the plant and the design of the building should be such that retaining kerbs may be provided without impeding normal movement and activities in the vicinity of the plant. With the development of modern methods of remote control, however, it is becoming increasingly possible to construct in the open air plant that had hitherto, in the interests of the workers' comfort, to be inside a building. This tendency is likely to bring about a considerable reduction in danger from fire and explosion.

The last example to be considered relates to a situation so frequently associated with bad accidents that great emphasis has had to be placed on the precautions. When a vessel has contained a flammable material and heat is to be applied to it for some purpose such as welding, brazing, soldering, or cutting, any flammable mixture that may be present in the vessel or that may be formed as a result of the application of the heat is almost certain to be ignited. Many fatal accidents have occurred from explosions caused in this manner. In one case a man had been instructed to cut open a drum that had contained a solid flammable ester—a waxy material. While he was cutting the steel bands round the drum, the heat of his torch caused residual material sticking to the inside of the drum to vaporize. By the time he had cut off the top of the drum an explosive concentration had formed inside the drum, and this was ignited by the flame of his torch. The man was killed by the explosion.

Before an operation of this sort is undertaken one must make certain that there is no flammable concentration inside the vessel, and that a flammable concentration cannot develop in the course of the work. To make sure that this is so, every trace of flammable material must be removed from the vessel. Sometimes it is sufficient to purge the vessel thoroughly with steam, but, when heavy oils and greases are present, the vessel may first have to be boiled out with alkali and then steamed. If there is any doubt concerning the adequacy of the treatment that a vessel has received, a test should be applied.

Conclusion

Accidents such as those described above have led the Factory Inspectorate to place special emphasis on certain precautions, but it should be unnecessary to add that these precautions are not emphasised to the exclusion of all others. To deal with all these, however, a much longer account would have to be written.

The manuscript of this paper was received on 20 *January*, 1960.

AN APPROACH TO THE PROBLEMS OF PROCESS HAZARDS IN PLANT DESIGN

By A. D. THACKARA, M.A., A.M.I.Mech.E.,* R. M. ROBB, B.Sc.,* and R. B. T. HALL-CRAGGS, M.A., A.M.I.Mech.E.*

SUMMARY

This paper deals with the work of a process safety department as a distinct unit in the engineering headquarters of a company involved in chemical engineering.

Introduction

'Process safety' is defined as the safeguarding of people in the first place and of productive capacity in the second place against breakdown of equipment caused by over-pressure, fire, or explosion, and also against the escape of dangerous materials or radiation.

Although such safeguards are part and parcel of all good engineering design, the authors' company has more than 30 factories throughout the world and may have more than a dozen major engineering construction projects simultaneously on hand: the directors have found the need for a special department to apply the required standards of safety and to see that these standards are maintained. Comparable departments were already established for boilers and power plant, metallurgy, buildings, and other branches of engineering.

The company manufacturers soaps, synthetic detergents, edible fats, cellulose, and other products.

Organisation

The company has a headquarters engineering division in the United States of America. This division undertakes the main development and construction work and also checks the work of the engineering departments in the factories, advising them as needed. The process safety department is one of the departments making up the division.

The British subsidiary company also has a headquarters engineering division doing the same thing for the factories in this country. It is in very close contact, technically, with the main division in the United States.

The Task Facing a Process Safety Department

The duties of a process safety department may be classified under three main headings:

1. For new construction: directing the engineering work in this respect.
2. For equipment in operation: checking the quality of inspection and maintenance.
3. For people: giving technical information, training, and propaganda.

Information

The department builds up its own library of technical and legal information. This gives the references for assessing the risks of fire and explosion in given conditions, and also the physical quantities on which to base calculations. In particular, it has assembled a *Process Safety Manual*. This book lays down all the procedures, as described later, and condenses and standardises the calculations which are usually needed. All factories receive this book.

Flow charts

When an installation is being designed, the process safety department keeps in continual touch with the development of the flow charts by the design engineers principally concerned. When the flow charts are complete, they carry the data about protective devices and the pressure ratings for all vessels and other equipment which result from the studies of the process safety department.

Summary

The work of the process safety department on any installation is assembled into a special manual which is handed to the factory operating and engineering staff on commissioning.

Inspection

As an over-riding check on the work of others, the process safety department undertakes its own inspection of the protective devices of an installation before it begins to operate.

Auditing of current operations

The process safety engineer of a factory has to see that safety devices are inspected and maintained. He also scrutinises changes to equipment for new hazards. The headquarters department sees that he uses the standard procedures for this and checks and reports on the work done by the factory staff.

Training

Besides training staff for the factories and for headquarters for this specialised work, there is need occasionally to bring it to the notice of other members of the engineering and operating staffs. This parallels the extensive propaganda on personal safety which has proved of very great value.

Detailed Procedure

The work regularly done by the process safety department is described in more detail under these headings:

General safety study.
Detailed safety study.
Rating the hazards.

*Thomas Hedley & Co. Limited, Newcastle upon Tyne.

Specifying protective measures.
Process safety summary.
Pre-start up inspection.
Checks on the work of the factories.
Training.

General safety study

During the design of an installation, the process materials, the chemical reactions, and the general concept of the proposed plant are studied. The research and development departments are asked to elicit dangerous characteristics of the materials in the process. The intention at this stage is to bring out the major potential sources of hazard. Typical points to be considered are:

Ignition of flammable gases and dusts due to sparks with the system.

Mixing of two materials giving rise to a high rate of liberation of heat (*e.g.* sodium and water).

Escape of hot flashing, toxic, corrosive, or flammable materials or radiation.

The possible occurrence of pressures greater than those produced by normal working.

It is essential that this general study should be done early. It will often result in recommendations which affect the concept of the plant, its location, layout, and cost. Explosion-prone sections of plant may need to be built in the open, or in areas with blast walls, vents, and sufficient ventilation. Special fire equipment may be required of which the design should be integrated with that of the process plant. The need for earthing pipe lines may affect choice of pipe materials and cost. Electrical installations may need to be flameproof.

The general safety study is a joint task for process safety and process equipment design.

The process safety department brings to this study a fund of company experience. It studies statutory regulations and the recommendations of outside bodies. It seeks advice from other companies about handling unfamiliar materials. Such help has been freely given and is highly appreciated. The literature is studied. Experimental work may be initiated for example to establish realistic flammability tests, or to test the effectiveness of explosion vents.

Detailed safety study

INITIAL PREPARATION OF HAZARD SHEETS

When the general safety study is complete the process equipment design department finalises the flow chart and layout (*e.g.* Fig. 1). The process safety department reviews the flow charts in complete detail, looking for potential sources of hazard.

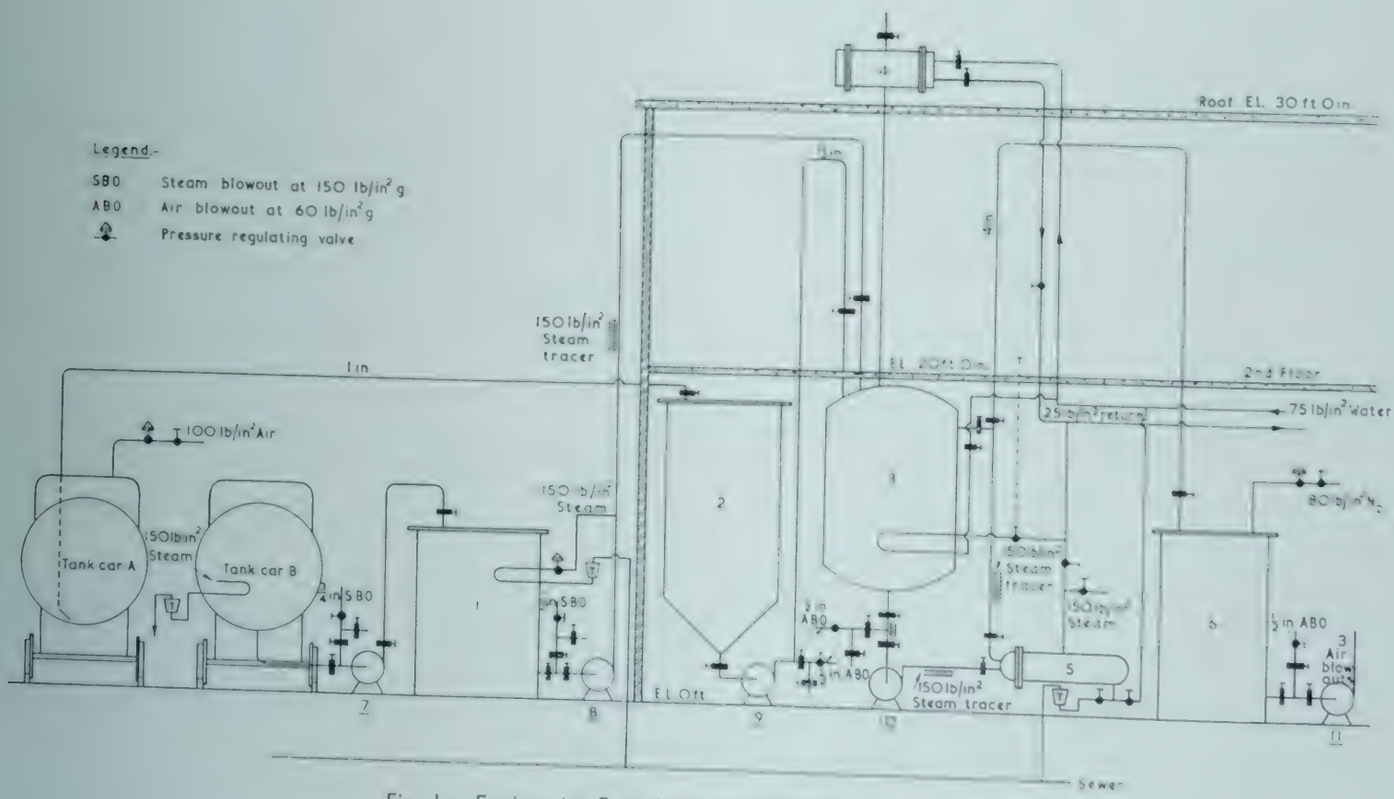

Fig. 1.—*Engineering flow chart prior to detailed safety study.*

A hazard sheet is prepared for each item or groups of items where a hazard exists which must carry certain key information:

Clear and positive identification of the item or items to which it refers.

Statement of maximum allowable pressure or vacuum.

The process safety engineer must satisfy himself that he has the right figures. If no proper calculations have been made, he must do them.

A list of the hazards to which the item may be exposed.

Space for hazard rating, which is described later.

Space for the specification of protective devices, described later.

Space for relevant calculations.

Fig. 2 (a & b) gives examples of hazard sheets. At this stage the centre and right hand columns would be empty.

This is the initial preparation of hazard sheets. Their completion is described later. The important first step is to recognise all the hazards; protecting against them is a separate matter. If they are not found they will not be guarded against.

CHECK LISTS

In probing for possible hazards, the process safety engineer uses a check list of possible sources.

Over-pressure is checked against several headings: for example ruptured tank coils, blow outs, thermal expansion of trapped liquids, condensation, chemical reaction, pumping pressures. All possible operating mistakes are considered. Fire and explosion hazards are similarly checked. Process materials may include flammable liquids, gases, or dusts. Compounds may be unstable. Ignition may come from open flame, electrical devices, lightning, static, addition of hot materials, or sparks from process furnaces.

ESCAPE OF HARMFUL MATERIALS OR RADIATION

Radiation is not a major factor in the authors' company, but radioactive sources are in use, and are included in the process safety department.

The possible escape of materials harmful to people is also noted. The design engineer and the people concerned directly with the safety of operation have the prime responsibility though the process safety engineer is closely concerned. The process safety engineer does make recommendations on vent capacity. If a flammable material may escape, he is directly concerned because there may be a fire or explosion hazard in the area.

HAZARD SHEET No.4.

EQUIPMENT TANK N° 2 DATE: 8/6/60

ENG. FLOW CHART _____ MAP 1·33 psig

MAV _____

HAZARD.

No.	DESCRIPTION	RATING	PROTECTION	
1.	27·5 lb/in² LIQUID PRESSURE FROM TANK CAR 'A'	A.1.	4in OVERFLOW	ST.106
2.	OVERPRESSURE FROM A.B.D AT PUMP N°9	A.1.	6in. VENT.	ST.107
3.	OVERPRESSURE DUE TO REVERSED FLOW FROM TANK 3.	A.2.	6in. VENT AND 4" OVERFLOW.	ST.106&7
4.	VACUUM PULLED BY PUMP N° 9	A.1.	6in. VENT.	ST.107
5.	27·5 lb/in² AIR PRESSURE FROM TANK CAR 'A'	A.1.	6in VENT.	ST.107

NOTE:-
THE SIZES OF VENTS AND OVERFLOWS ARE CALCULATED FROM METHODS AND DATA WHICH ARE STANDARDIZED IN THE "PROCESS SAFETY MANUAL."

Fig. 2a.—*Completed hazard sheet*

HAZARD SHEET No.7.

DATE: 8/6/60
SHELL 150 lb/in²
MAP TUBES 150 lb/in²
MAV. FULL VACUUM.

EQUIPMENT HEAT EXCHANGER Nº 5
ENG. FLOW CHART

HAZARD			
No.	DESCRIPTION	RATING	PROTECTION
1.	OVERPRESSURE FROM 150 lb/in² STEAM IN SHELL	A1.	ADEQUATE M.A.P.
2.	DITTO. IN TUBES.	A.1.	DITTO
3.	THERMAL EXP. OF VALVED OFF CONTENTS IN TUBES.	A.2.	½in R/V SET AT 150 lb/in² (STAINLESS STEEL) SI 110
4	OVERPRESSURE FROM PUMP 10	A.2.	ADEQUATE M.A.P.
5.	" " ½" A.B.Q. AT PUMP 10.	A.3.	DITTO
6.	VACUUM CAUSED BY CONDENSATION OF VAPOURS.	A2.	ADEQUATE M.A.V.
7.	80 lb/in² N_2 FROM TANK Nº 6.	A.3.	ADEQUATE M.A.P.
8.	THERMAL EXP. OF SHELL.	A.2.	½in. R/V. SET AT 150 lb/in² SI. 111
9.	VACUUM CAUSED BY PUMP 11.	A.2	ADEQUATE M.A.V.
10.	OVERPRESSURE FROM REACTOR 3.	A 3	ADEQUATE M.A.P.
11.	FLASHED STEAM FROM STOCK BLOWING INTO WATER SYSTEM DUE TO TUBE RUPTURE	A.1.	VALVE-FREE 25 lb/in² WATER RETURN LINE.
12	100 lb/in² AIR BLOWING INTO WATER SYSTEM DUE TO TUBE RUPTURE.	A.1	DITTO
13.	STEAM INTO WATER SYSTEM DUE TO COMMON CONNECTIONS AT HEAT EXCHANGER.	A.1.	2/2 WAY 3-PORT COCKS INTERLOCKED SI. 113

Fig. 2b.—*Completed hazard sheet*

CORROSION

The process safety department, while keeping corrosion in mind, does not carry the direct responsibility for ensuring that items of plant are constructed of the right materials. This responsibility is assigned to the process equipment designers.

PRESSURE VESSELS

A separate technical check is made on all pressure vessels for correct design and choice of material. A separate programme of inspection and auditing ensures proper maintenance of pressure vessels and controls changes of design.

The operating managers are responsible for seeing that corrosive process materials are not, through mistakes in operation, fed into vessels unsuited to them. The process safety department does not protect against mal-operation of this kind, unless there is a risk of over-pressure, fire, or explosion.

Rating the hazards

APPROACH

Once a hazard is recognised there are often many courses of action which will remove it or minimise its effects. A uniform level of protection must be applied to many diverse plants over a period of years. If there is under-protection there is danger. If there is over-protection, money is wasted, and moreover all protective measures may be brought into disrepute because some will be seen to be unnecessary. To help decide the course of action the facts are assembled logically:

How precisely might an incident develop from each particular hazard?

How likely is the incident to happen?

How serious would the incident be if it happened?

The likelihood and seriousness of result are considered separately.

This is one of the key points.

Likelihood is expressed as:

1—Likely
2—Possible
3—Remote

Seriousness is expressed as:

A—Very serious
B—Serious
C—Less serious

To help to rate the hazard in a reasonably uniform and simple manner, examples of each rating are built up, though it is realised there is a need for informed judgment supported by the company experience.

RATING LIKELIHOOD

The cause of an incident may be broadly classified as mechanical or operational failure. Typical ratings are given in Table I.

TABLE I—*Rating of Hazards.*

Likelihood of hazard	*Mechanical hazard*	*Operational hazard*
1. Likely	Failure of a tube of a heat exchanger which is handling corrosive material. Passing valve.	Opening one valve to source of pressure.
2. Possible	Disintegration of two non-return valves in series.	Opening two or more valves in series to a source of pressure.
	Failure of a tube of a heat exchanger which is handling non-corrosive material.	Valve off a vessel completely (two or more valves).
3. Remote	Tank coil rupture. Isolating valve breakage.	Closing a number of valves on down-stream side of vessel.
Rating seriousness		
A. Very serious	Failure of any pressure vessel containing air or gas. Failure of a pressure vessel containing strongly corrosive liquid. Explosion or fire.	
B. Serious	Momentary overpressure of pressure vessel containing air or gas by more than 100 per cent. Failure of a vessel or pump resulting in fairly large losses of not particularly hazardous materials.	
C. Less serious	Tanks with weak flat tops which will fail under overpressure before the shell. Failure of vessel or pump containing non-hazardous material, small losses.	

The combined rating, **A1, B3, C2,** etc., is noted on the hazard sheet and this helps in deciding the extent of the protection which will be specified.

Specifying protective measures

APPROACH

The process safety engineer now has a qualitative picture of the hazards, how likely incidents are to develop, and how serious the consequences might be. Major recommendations will have been made during the general study. Therefore by this time it is normally possible to protect the plant by specifying protective devices and/or by imposing restrictions. The ratings offer a guide in deciding what protective devices or other measures are justified.

Where practicable, all **A** hazards (very serious) and **B1** and **B2** (serious and possible) and **C1** (less serious but likely) are positively guarded against: others are not, *i.e.* in the case of ratings **B3, C2,** and **C3** good operation is relied upon.

This approach is relatively easy to apply to over-pressure hazards and it is used extensively for this purpose. Fire and explosion are usually **A**, and are normally difficult to guard against completely, so that their study in particular requires the exercise of informed judgment. Nevertheless, the general approach of judging likelihood and consequence in turn is valuable here too.

Technical solutions to protection problems are not included in this paper but general practice can be illustrated by the points given below.

Example of practice

Overpressure or vacuum

a. Assume that all pressure sources rated **A1, A2, A3, B1, B2,** can come into effect together.

b. If natural vents are inadequate, first seek to restrict the sources of pressure.

c. If relieving devices are needed establish the quantity which each must handle.

d. If the rate of build up of pressure or vacuum from a known source is uncertain, establish it, by calculation, reference to published data, or test.

e. When **B3, C2,** or **C3** hazards are noted, the plant operator is relied upon but will specify restrictions clearly in the process safety summary.

f. Certain vessels are exempted from the need for special relief devices.

Fire

1. The normal codes and regulations are complied with except where company requirements are more stringent.

2. The aim is to prevent fires. A closed system, or separate location may be provided. Sources of ignition can often be removed, *e.g.*

Pressurised or Buxton certified electrical fixtures.
No open flame.
Spark-proof tools and chains.

Good ventilation can prevent dangerous concentrations of vapours.

3. The spread of fire is limited by dykes, fire walls, or space.

4. The best means of fighting a fire are provided.

5. The total quantity of flammable materials present may be restricted.

Explosion

The practices illustrated under Fire generally apply. In addition:

1. 'Allowable pressure' is determined by yield stress rather than design stress.

2. If the equipment cannot stand the pressure generated by an explosion the maximum possible rate of pressure rise is determined and vents provided. If venting is impracticable the likelihood of the maximum rate of rise being attained, as compared with a lower figure is considered. Structural strengthening may be needed. Normally, major items of equipment are so studied at the general safety study.

COMPLETION OF HAZARD SHEETS

The specification of safety devices and other measures is noted on each hazard sheet. Calculations and reasons are included.

Examples of completed hazard sheets are given in Fig. 2 (a & b).

SAFETY FLOW CHART

The safety flow chart is the equipment flow chart which has been prepared by the process design department, but with the work of the process safety department added to it. Compare Fig. 3 with Fig. 1.

The completed flow chart is the key document for the listing design and procurement of all equipment and material and subsequent testing. The safety equipment is included with the rest.

Process safety summary

The process safety department prepares a 'Process Safety Summary' for each project. Its purpose is to present important information to the engineering and operating people concerned, and to record information for future reference. The summary comprises:

1. General considerations

This section contains a general discussion of the main hazards, together with the means of protection. It also contains a reference to any unusual circumstances or hazards encountered in the study, together with a short summary of hazards to personnel, including precautions which should be taken in the event of injury from unfamiliar chemicals.

2. Equipment limitations

This section includes a note of any safety compromises, any hazards which are not automatically protected against, and any limitations of the equipment. It may contain instructions on mode of operation. This is an important section, particularly where subsequent changes of process are likely.

3. Safety notes and inspection procedures

This comprises the complete list and description of all the safety items specified and itemised in the study, together with guidance on the frequency of inspection and the testing procedures to be adopted for all the safety devices.

4. Hazard sheets and calculations

The process safety engineer puts on record the basis of his decisions on type of protection, sizing of protective devices, and methods of calculation.

5. Specifications

Specifications for buying protective devices, drawings, manufacturer's instructions, and similar information.

6. Safety flow chart

This is the engineering flow chart marked up with safety devices and symbols which was mentioned earlier. An example is given in Fig. 3.

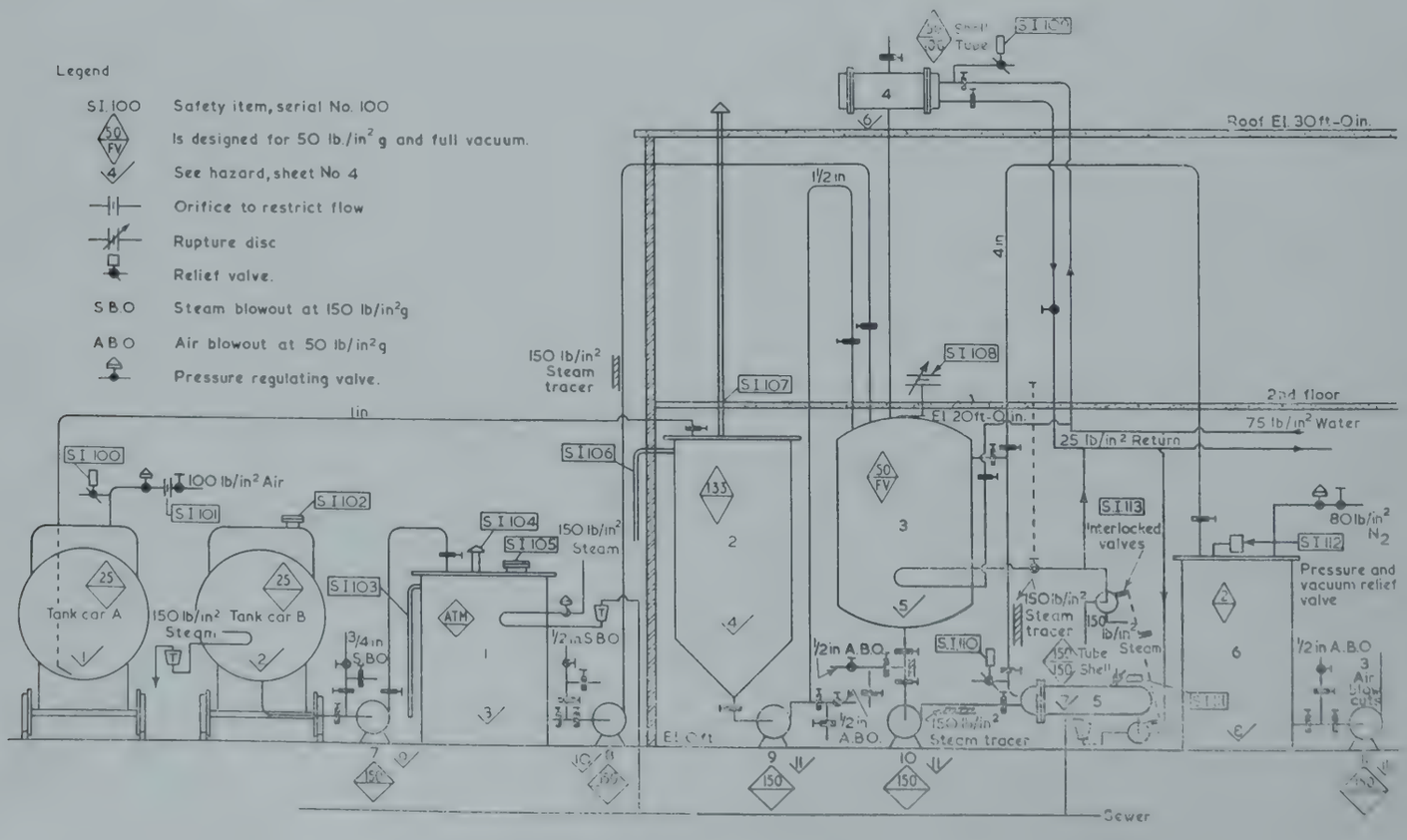

Fig. 3.—*Safety flow chart*

7. Design changes

In this section are noted all alterations to the equipment after it has been commissioned. Such alterations must be reviewed by the factory's own process safety engineer before they are undertaken, and recorded by him here for the benefit of future audits.

Pre-start up inspections

The process safety department makes a physical inspection of the plant before and during commissioning. They check that every safety device shown on the safety flow chart is present, properly installed, and tested. They hand over a copy of process safety summary to the factory, and in doing so, they discuss personally with the operating people all special features, particularly equipment limitations.

Checks on the work of the factories

The process safety engineer at each factory is given a series of explicit instructions to do the following:

1. See that all safety devices are tested regularly.
2. Keep records in standard form of tests and maintenance work.
3. Check and approve changes to equipment from the point of view of process safety.
4. Examine and report on any accident, or incident which might have led to an accident, on process equipment. Fig. 4 gives an example of a report on such an incident.
5. Study afresh each department of the factory in full detail using basically the methods that have been described above in connection with new installations. This uncovers any feature which has fallen short of the required standards of safety. Each department gets re-studied every four years. The process safety department of engineering division carries out an audit every two years on the work at each factory and reports the findings. The department receives copies of all incident reports. It discusses with the factory staff all proposals arising out of the four-yearly review. Less formal contacts are frequent.

Training

Training is provided at headquarters for engineers who will

T.H. & Co No: 1790/1

PROCESS SAFETY INCIDENT REPORT.

PLANT MANCHESTER

DEPARTMENT C.S.M.

DATE OF OCCURRENCE 8TH MARCH 1958

[X] DAMAGE FROM PROCESS SAFETY HAZARD

REASON FOR REPORT -

[ ] HAZARDOUS INCIDENT BUT DAMAGE AVERTED

[ ] TROUBLE WITH SAFETY DEVICES

ANSWER AS MANY QUESTIONS AS POSSIBLE.

BRIEF DESCRIPTION OF OCCURRENCE C.52 TANK TOP COLLAPSED DUE TO VACUUM.

M.A.P. OF ANY DAMAGED EQUIPMENT 7·1 lb/in² abs (CONE TOP)

BASIC HAZARD INVOLVED VACUUM

BASIC CAUSE OF INCIDENT VACUUM RELIEF NOT FITTED

DESCRIBE SEQUENCE OF EVENTS PERTINENT TO INCIDENT. (SUCH AS OPERATING FACTORS, REMOVAL OR FAILURE OF SAFETY DEVICE, ETC) TANK HAD SMALL CHARGE & STEAM COILS ON. THE TANK WAS THEN RECHARGED & STEAM FLASHED OFF. THIS STEAM CONDENSED FORMING A VACUUM & THE TANK TOP COLLAPSED

WAS ANYONE INJURED NO DESCRIBE INJURIES SUSTAINED

EQUIPMENT SHUT DOWN NO DOWN HOURS

ROUGH COST ESTIMATE: (EXCLUSIVE OF PERSONNEL INJURY AND DOWNTIME) £20

WHAT CORRECTIVE MEASURES ARE RECOMMENDED TO PREVENT A RECURRENCE? FIT VENT TO TOP OF TANK

DISTRIBUTION -
DIRECTOR OF MANUFACTURE; ENG. DIV (P.S.E)
PLANT ENG; FILE

SIGNATURE CB CLOUGH TITLE PROCESS SAFETY ENGINEER

Fig. 4.—*Typical report of minor factory incident*

undertake process safety work. An intensive course, lasting a week, is repeated when needed. This is largely based on the process safety manual and explains in detail the methods of working contained therein. Practical demonstrations of studies and calculations are undertaken. Infrequently, as needed by extensions and promotions and the resulting arrival of new men on the operating and engineering staff of the factories, formal lectures are held explaining the work of the process safety department, the reasons why it was founded, and the parts which the company expects other members of its staff to play in helping it to further its ends.

Characteristics and Value of the Process Safety Programme

The paper has concentrated on an approach to the problem of process hazards in the design of new plant. This approach is part of a rather wider programme of work.

Characteristics of programme

Important characteristics of this programme are that:

It is applicable to a wide variety of processes and equipment.

It helps to secure a known standard of safety throughout a number of plants and for the full life of the plant.

It is thorough, reveals the less apparent hazards, and attends to important detail.

It makes specialised experience and knowledge widely available:

Cost and value of programme

The cost of the programme is appreciable. A number of engineers is needed to operate it. Safety measures generally cost money.

However, tangible advantages accrue:

The programme helps the company to provide safe working conditions.

It enables the company to move with assurance into new fields. Freedom from major failures during the early stages of operation can be crucial to the successful exploitation of a market. Experience has been that hazards, particularly on unfamiliar plants, are not revealed by normal engineering checks.

It provides basic reliability during the life of the plant. The need for standby plant is reduced. Production can be scheduled with confidence so that excessive stocks of finished product can be avoided.

Proper understanding of the risks may permit reduction of the factor of safety provided against the unknown, and hence reduce capital cost.

The programme is justified not only on ethical grounds but also in terms of money.

Conclusion

The approach outlined is but one part of the effort required to attain the objectives of safety and reliability in a factory as a whole. Similar effort must be applied in other fields including safety of personnel, steam and power, buildings and structures, key vessels, and mechanical plant. Conversely, the procedures outlined will be valueless unless the will to use them exists. Fostering and preserving the will to use them is a task for management.

Acknowledgments

The authors, on behalf of Thomas Hedley & Co. Limited, Newcastle-on-Tyne, wish to acknowledge the help of the parent company, Procter & Gamble of Cincinnati, Ohio, who developed the programme, helped to apply it in England, and who have given them permission to publish this paper.

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AUTOMATIC CONTROL AND INSTRUMENTATION FOR HAZARDOUS PROCESSES

By A. H. ISAAC, B.Sc., A.M.I.Chem.E.*

SUMMARY

The appropriate use of instrumentation can make a substantial contribution to the safe operation of processes. An analysis of some of the sources of hazardous conditions that can arise in plant indicates the nature of protection that instruments can provide. This can be achieved only by emphasis on safety throughout design and by attention to details. The use of automatic process control itself may introduce special hazards that must be anticipated and overcome. Safety and alarm systems can be used to provide warning of dangerous conditions and to shut down the plant automatically when this is essential.

Introduction

The most innocuous of chemical plants may give rise to accidents under exceptional operating conditions. The consequences of such occurrences are naturally more serious where the plant is handling flammable or toxic materials or where it is subject to excessive corrosion and extremes of pressure or temperature. The correct incorporation of instrumentation and automatic control in the plant design can avoid this danger and minimise the risks arising from such conditions. Such hazards may jeopardize the plant, the process, the product, and the personnel.

In any particular case one or other of these categories may be the most serious; in others several or all may be involved. It is convenient to consider some classification of this type to allocate the appropriate significance to precautions that must be taken. For example, overheating in a batch polymerisation process may not involve any hazard to operators or endanger the plant but may well result in a ruined batch of high-value product. In a similar way rupture of a bursting disc can adequately protect the plant but at the risk of releasing poisonous or flammable materials which may both endanger the operating staff and shut down the process.

Clearly, a large number of types of equipment may contribute to safety in plant operation and could be classified as instrumentation. It is proposed to exclude from this paper such devices as safety valves, non-return valves, bursting discs, safety seals, and torque shear pins which are essentially limiting devices. Consideration must also necessarily be extremely brief in respect of items that are strictly limited to " spot testing " or general laboratory supervision. If principal consideration is given to instruments on continuously operating plant, it should be understood that such items are used as complementary to the above. Some of the implications of abnormal conditions on automatically controlled plant are considered in relation to safety.

Sources of Hazard in Plant Operation—Protection by Instruments

A brief consideration of some of the sources of hazardous conditions that can arise serves to indicate the way in which instrumentation is applied to reduce or avoid the occurrence of serious dangers.

Breakdown or failure of plant items

The problem of breakdown or failure of plant items lies essentially in anticipating incipient failure of equipment. Instruments cannot indicate a potential breakdown of a pressure vessel under operating conditions: however, the examination and inspection of pressure equipment by various means of non-destructive testing is being increasingly used. Routine examination of condenser tube walls, pressure-vessel shells, and similar units as a check on corrosion is a valuable protection but these techniques are not applicable for continuous service.

In the protection of rotating machinery the measurement of bearing temperatures, lubricating-oil pressures, and the continuous monitoring of vibration conditions are widely applied and serve in their turn to indicate the development of bearing failure and similar conditions before this has produced any serious consequences. Direct measurements of shaft-torque using strain gauges and other techniques serve to protect large agitators and centrifugal machines against overloading.

In the case of heat transfer equipment protection lies in ensuring even heat distribution and the avoidance of " hot spots " which may give rise to breakdowns. The measurement of tube wall temperatures in water-tube boilers is a good example of this technique. In a similar way differential pressure measurements across a tube-still coil will indicate coking conditions which can result in a burn-out.

Breakdown due to corrosion is common and can be prevented in many cases by measurement and control of the environment giving rise to the attack. Examples of this include recording the flue-gas temperature of a boiler as a guide to prevent cooling to dewpoint causing deposition of acid liquors in a steel stack. A more elementary case is that of limiting the water-side temperature of gas coolers with galvanised tubes to prevent attack of the zinc. Serious hazards can arise in closed condensate-return systems for boiler feed. If the condensate is trapped from heaters handling corrosive liquids any leakage of process fluid into the heater steam space can result in corrosive feed being passed to the boiler with potentially very serious consequences. Adequate conductivity monitoring of condensate return lines

* Foxboro-Yoxall Ltd., Redhill, Surrey.

can avoid this by automatically diverting contaminated streams with a suitable alarm.

Interruption of services and supplies

Plants are designed to operate satisfactorily in the presence of certain services, *e.g.* steam at specified pressures, water at particular temperatures, electrical power supplies of certain characteristics, fuel supplies, etc. In the event of failure or interruption of such services plants are operating under seriously abnormal conditions and this may give rise to hazardous conditions. A suitable degree of instrumentation must be provided both to give warning of the failures and possibly to introduce standby supplies or alternative methods of operation. For example, a steam feed-pump can be started by the fall of pressure which a power failure will cause in the delivery of an electric pump.

Failure of feed flows to processes can be dangerous, particularly with heat exchange equipment. The differential temperatures across heat-exchange surfaces will be very different when there is no flow past these than under design operating conditions. Water boiling in the shells of condensers or liquors freezing in brine coolers at very low flows are typical cases.

In many problems of this type the consequences of failure are so serious that interlocked shut-down mechanisms must be included to safeguard the plant.

Departure from design operating conditions

No processes operated under design conditions are inherently hazardous. However, dependent upon the nature of the process or plant, even minor departures from these conditions may have serious results. Such departures may be caused by extraneous circumstances, by inadequate supervision of plant operation, or even by attempting to operate plants at conditions for which they have not been designed. One case of this in which instrumentation plays a very significant part is the use of flame failure devices on oil or gas burning furnaces. A trace of water in the fuel or some other momentary interruption of fuel supply may be sufficient to extinguish the flame. In the lack of any immediate action the furnace will rapidly fill with an explosive mixture constituting a very serious hazard. Flame failure devices properly applied can shut down the plant and provide suitable warning to the operator.

In a similar category lies a wide range of catalytic vapour phase reactions such as the oxidation of benzene, naphthalene, methyl alcohol, and ammonia which are carried out on a large scale. The explosive properties of the vapour-air mixtures limits operation to an extremely narrow band of compositions if the danger of explosion is to be avoided. Very precise control over the proportions must be maintained and a detailed knowledge of any departure from these conditions is of great significance. Not only may the plant and personnel be jeopardized by serious explosion hazards but, for example, in the case of nitric acid or formaldehyde oxidations even a minor departure from appropriate proportions is sufficient to destroy the high-value metallic catalyst bed. For this reason it is usual to provide warning devices both for the departure of the air vapour flow ratio from normal, either high or low, and for excessive temperatures in the catalyst bed.

Mal-operation of plant

Manually operated plant is inevitably subject to the vagaries and characteristics of the operating staff and consequently may be subjected to serious hazard due to their inadequate instruction, inattention or error. In fact, a large majority of accidents on chemical plant are ultimately accountable to human failure. The use of suitable measurement and alarm equipment serves to assist the operator in this respect and to enable him to take appropriate steps in any situation. Recording instruments provide a check of conditions which enable errors to be rectified and assist analysis of the situation by management. In the ultimate, the use of automatic process control removes much of the responsibility for detailed operation from the operator but it must be appreciated that the most hazardous period on such plants is during start up, when the automatic control may not be in full command of the situation.

In batch processes where a complex sequence of operations must be followed suitable interlocks and cycle operators serve to avoid the possibility of omitting a step or confusing the procedure. Mal-operation can extend to gross interference with the plant items as installed. For example, the screwing down of safety valves to prevent leakage, the wiring out of alarms and overload trips and disconnection of fire appliances. Suitable alarms and indicating lamps can avoid some of these but in the extreme they are essentially management problems. One common source of hazard arises in the filling of storage tanks with toxic or flammable liquids. Spillage due to overfilling of these can be avoided by reliable and accurate level-measuring equipment with automatic cut-off and alarms where appropriate.

Hazards inherent in the process

A large number of processes inherently possess potentially hazardous characteristics and the plant design accepts this. The instrumentation requirement is for adequate information on conditions to avoid the basically hazardous components creating a serious menace. Mention has already been made of the explosive or toxic properties of many chemical reactants. For adequate supervision of handling, processing, and disposal of such materials measurement and observation of their properties must be made at all stages.

For example, in the disposal of cyanide effluents by oxidation to cyanates the completion of reaction is observed and the process controlled by continuous measurements of the oxidation-reduction potential of the system. Other hazards arise from the physical conditions ruling in the plant and clearly where these involve excessive pressures and temperatures, there is a tendency to work closer to the limiting performance of the plant materials. Regulation of water to superheater control tubes, maintenance of feed to tube-still heaters, and protection of furnace linings from overheating by roof temperature measurements are some typical examples.

Plant Design for Hazardous Processes—Instrumentation Considerations

The above comments serve to indicate the type and origin of hazardous conditions that can arise in any plant and the contribution instrumentation can make in avoiding them. In the design of plant for processes known to exhibit hazardous characteristics, an analysis of this type must be combined with a review of the relevant instrumentation considerations. Some of these will be mentioned.

Measurement

To maintain the operation of plant in a safe state a continuous provision of information is required on the operating

conditions at various points in the plant. Essentially this implies measurement at these locations and the adequate presentation of data on pressures, temperatures, flows, levels, analytical quality, and other properties. In this way the operator is in a position to assess precisely the conditions and circumstances not only of the significant operating regions of the plant but also at extraneous points and in ancillary units to ensure that hazardous conditions do not arise in these.

The choice of the significant factors for measurement on any particular plant must necessarily be an individual one. Such instrumentation may be primarily incorporated for protection against danger but may also have other functions which would support its application, *e.g.* costing, production, process operation, etc.

Instrument location

Modern instrumentation permits the transmission of information over relatively long distances and this removes the necessity for the operator's presence in the immediate vicinity of the plant units. In particular in the case of toxic reactants where there must always be the danger of slight leakages, such a precaution is obviously desirable and in the case of highly explosive or radio-active reactions it is essential. In an extensive plant it has the added advantage of centralising information to one locality so that the operator can rapidly assess the general operating conditions on the plant. The operation of the plant from a remote location places a great emphasis on the completeness and reliability of the instrument readings.

It should not necessarily be assumed however that a hazardous process is always best operated remotely. In particular where reactions are only partially instrumented or automatically controlled there is every reason for grouping the measuring equipment together but at a point immediately adjacent to the reaction equipment. This means that the operator is in a position to supervise visually and operate manually the reaction equipment whilst having the added advantage of specific measurements made available to him. Many batch operations are in this category. In certain cases visual examination may appear to be essential, *e.g.* condition of solids on conveyor belts, shape and characteristics of flames and sprays, discharge of solids from chutes, etc. Undoubtedly these present a challenge but in a number of cases they have been successfully solved by the use of closed-circuit television systems. These are, however, relatively costly and elaborate and their use is justified only where no other solution is available.

Instrument mounting

The display of information on a panel may be either conventional or graphic. In the former the basic critical measurements are grouped at one location on the panel with the incidental indications around these arranged generally in relation to the plant units they serve. The graphic display presents the information in the form of a flow sheet of the process with the various indications shown at the appropriate points in this. This arrangement is said by a number of users to overcome the problem of operational errors when hazardous situations arise by its inherent demonstration of the interrelation and interaction of the various units. The presentation of alarms is covered below.

Reliability of measurement

The value of protection derived from instrument readings depends on the attention given at the design stage to the performance of the measuring equipment and its characteristics. For example, due allowance must be made for the time of response of temperature measuring instruments when considering transient temperature peaks. What appears from a record to be a peak of 10° lasting 4 minutes may well have reached 15° or more but the full amplitude of the peak has been lost due to the attentuation of the thermometer and its associated pocket. This also applies to many types of analytical equipment since their time of response is slow and they may appear to show incorrect values when conditions are changing rapidly. Dangerous conditions can therefore develop without any indication of their occurrence, unless the measuring device performance is matched to that demanded under alarm conditions.

Another significant factor in the potential reliability of any measurement is the problem of location of the sensitive element or the sampling point for analytical equipment. Temperature measurements in catalyst beds, furnaces, or nuclear-reactor blocks can give widely differing values dependent upon location, and great care must be used in the original positioning to yield satisfactory results. The fuel-element failure in the Sellafield nuclear reactor was a good example of this because it happened to be in a fuel channel not incorporating a thermocouple so that the excessive temperature was not observed.

Control

In addition to information on the operation of the plant it is of course reasonable to provide some means for the operator to counteract the development of hazardous conditions when these are indicated. This may be achieved by the use of remotely operated valves or pumps, the actuation of fire sprinkler systems, dump-valves, etc. In the ultimate, automatic control clearly has much to offer in applications of this type. Not only does it permit the operation of the plant with minimum possibilities of human error but fundamentally makes corrective action more evenly and more gently and with less over-shoot than is possible with the human operator. In many hazardous processes, such as catalytic cracking, for example, this if of such great consequence that the processes are virtually uncontrollable by manual means. The use of automatic control, however, introduces itself a number of potential hazards that must be considered.

Safety Considerations in the Use of Automatic Process Control

As mentioned above, the purpose of automatic control on hazardous plants is to retain the variables at safe operating values. At the same time the use of automatic control on plant implies only a limited degree of routine supervision by the operator and therefore more serious consequences if for any reason the plant variables should deviate substantially from the desired values. Automatic control loops are usually established and designed for a normal range of operating conditions only. Their rangeability may well be considerable but will limit the flexibility to deal with exceptional operating conditions that may arise due to extraneous causes. The automatic controller is a blind device with no power of discretion in these circumstances if faults give rise to unusual operating conditions an automatic controller can aggravate the situation.

Since deviation from control may imply the development of hazardous conditions it is worth analysing some of the reasons which will cause variables to deviate substantially although they are under the general command of an automatic controller.

Excessive demands

The imposition of operating requirements beyond the limiting performance of the plant units means that control valves are completely opened, surge tanks overflow, distillation columns prime, etc. Needless to say, under such conditions the plant cannot continue to operate in a normal condition. The reasons for these limitations being achieved may be as mentioned above, be due to faulty operation, unusual operating demands, or limitations due to failure of some item in the plant equipment.

To avoid these problems the maximum flexibility must be provided in the basic-control system-design. This can be greatly increased by the use of sequenced control valves, cascade control systems, and other arrangements. Auto-selector control provides good protection in such cases as flow-controlled pumps where the level in the suction pump over-rides the flow control to protect the pump against the danger of running dry.

To take care of exceptional circumstances occurring on the plant, particularly during the start-up phase, most automatic controllers are provided with suitable automatic-to-manual transfer so that normal type remote/manual operation can be carried on when the process or the plant is not operating under anticipated design conditions and where the control systems provided might lead to dangerous situations.

Failure of controlled flow

Failure of controlled flow is a self-evident condition where for example failure of the cooling water to a heat exchanger or an inadequate steam pressure to a heater must result in deviation from control. To avoid dangerous conditions as a consequence of such deviations, suitable alarms must be used. One case is worth mentioning. In controlling the ratio of gas to air fed to burners it is usual to hold the gas in a fixed ratio to the independent air flow. This is because of the danger of losing air due to fan-power failure. With this system zero air flow will call for reduction of gas flow to zero under ratio control thus avoiding the production of a gas-rich explosive mixture.

Transient disturbances

The case of transient disturbances is an extension of the case of excessive demand and covers those cases where demands are made upon the plant that are in the long term no greater than the basic plant design is capable of handling, but which dynamically occur at faster rates, or give rise to transient disturbances through the system at such a rate, that it is temporarily overloaded and cannot respond in a stable manner. The limitation is the long time-constant of the plant.

Mechanical failure of plant

Obvious examples of mechanical failure of plant are those of burnt-out heater tubes and blocked lines. Control must suffer and may aggravate the failure once it has occurred. For example, a temperature-controlled gas-fired heater coil will open the gas valve wide if the coil ruptures and flow past the thermometer bulb ceases.

Saturation conditions or instabilities arising from the control equipment

Poor controller adjustment or inadequate and incorrect control loop design can give rise either to instabilities in loop behaviour or to saturation of some point of the loop. This means that a measurement reaches the extremes of its range or the control-valve travels to one of its limits. An example arises in the start-up of a batch reactor under temperature control. The temperature is bound to over-shoot because of saturation of the integral term which means that control does not start until the set-point is exceeded. It can be avoided by the use of an integral cut-out mechanism.

Failure of instrument power supplies

Pneumatic control valves normally have a fail-safe sense, since they are spring-opposed. In a number of cases it will not be possible to decide, however, whether a control valve should open or close on air failure and a safety lock or stay-put mechanism can be used. The gas collector main on a coke-oven battery is a good example. Even such devices are not entirely safe since clearly a safety-lock will only retain a control valve in the same position as it was at the moment of failure. Frequently such conditions as lead to failure are exceptional and the valve may well have been at an extreme position in the course of making correction for some disturbed conditions.

Where pneumatic transmission is used signal failure also may have a safe sense. Since air-failure may be a local situation only, it can fail at the transmitter but not at the valve. For example, if a temperature controller is used on a gas-fired furnace and is based on a normal type pneumatic transmitter where an air signal of 15 lb/in^2 corresponds to maximum temperature and 3 lb/in^2 to minimum temperature, air-failure at the transmitter will appear to the controller like a low-temperature condition. This will increase the supply to the burners to maximum in an attempt to correct this condition. This can cause irreparable damage to the heater and must be avoided by using reverse-signal transmitters.

Mechanical failure of the measurement or control equipment

Mechanical failure will generally occur only as a result of exceptional conditions such as over-range of the measurement, excessive corrosion, etc. It is apparent that a factor of safety in quality and design of equipment must be considered in setting up individual control loops, installation, and the selection of the mechanical components. An example of a safety feature is the " burn out " device used on potentiometric temperature controllers. This serves to simulate a high temperature condition when the thermocouple goes open circuit, as it will if the pocket burns through. This causes the control valve to shut to a safe condition.

Safety and Alarm Systems

General

An alarm system serves to draw attention to the presence of a fault or the development of a potentially dangerous value of any variable on the plant. It must also identify the nature and location of the hazardous condition. A complete safety system will, by means of an interlock circuit, automatically shut down all or part of a plant under any alarm condition or combination of such conditions.

These systems are based on measured process variables and should be distinguished from pilot lamps or tell-tale indicators, which are essentially running lights indicating the operation of motors, agitators, and the position of isolating valves. They are initiated by relays, starters, and limit switches associated with the equipment concerned.

A simple alarm system comprises, therefore, an initiation device, relay, presentation and display means. Complex

systems will also include interlocks and shut-down devices. These are considered individually.

Initiation

The basic initiation of alarm systems utilises a sensitive detecting device which can be set to operate at some predetermined value of the measured variable. Since the presentation of the alarm is nearly always in the form of electric signal lamps, bells, etc., contacts are incorporated in the device. Very high reliability is essential and mercury switch type contacts are therefore preferred. In order to fail-safe in the event of power failure such units are usually arranged to open, not close, circuit on alarm conditions.

The actuation of the alarm device must be from some measurement of the variable concerned. This may be the same basic measuring device that serves to provide a signal for recording or control, *e.g.*, mounted in a temperature recorder or connected to the output of a flow transmitter. It is possible to adjust the point at which the alarm trips. For the highest degree of safety the alarm should be based on an independent measuring device using a different method of measurement, a separate plant connection, and an isolated power system from that actuating the basic plant operation and control equipment. Only in the most critical duties will this be followed throughout since it implies duplication of most of the measurements on the plant.

The commonest form of initiation device used with pneumatic transmission systems is a high-quality pressure switch connected into the output of the pneumatic transmitter. Isolating valves in the transmission line permit servicing of the controller or recorder whilst retaining the alarm in service.

Relay system

In all but the very simplest alarm systems it is necessary to include an intermediate relay system between the initiation and the presentation. This permits the interpretation of initiation contact-action to a form suitable for the presentation and display equipment. At this point facilities for alarm testing, audible alarm actuation, and cancellation and the introduction of an intermittent power supply for " flashing " presentations is possible. The relay systems may be centralised serving all alarm points on a plant, or they may be in the form of self-contained individual units for each alarm system. In some cases they are combined with the signal lights and switches in a single housing.

Presentation and display

There is a wide variety of means by which the operator can be informed of the existence of hazardous conditions. The most immediate response is produced to an audible device such as a bell, siren, or buzzer. It is preferable that only one type should be used although several units may be located at different points of the plant to attract the operator's attention to the visual display. This serves to discriminate which of the particular alarm conditions has been exceeded. Consideration must be given to audibility particularly where much extraneous noise exists, for example in compressor houses and mixing rooms they must be immediately discriminated from any other audible systems used on the plant. In many cases the audible alarm may serve only as a warning of changing conditions that are not themselves immediately hazardous. For this reason corrective action may take some time and it is essential that a cancellation system is provided to permit the operator to silence the alarm during this period but which will keep the audible unit available for any other alarm condition. Such a system is illustrated in Fig. 1.

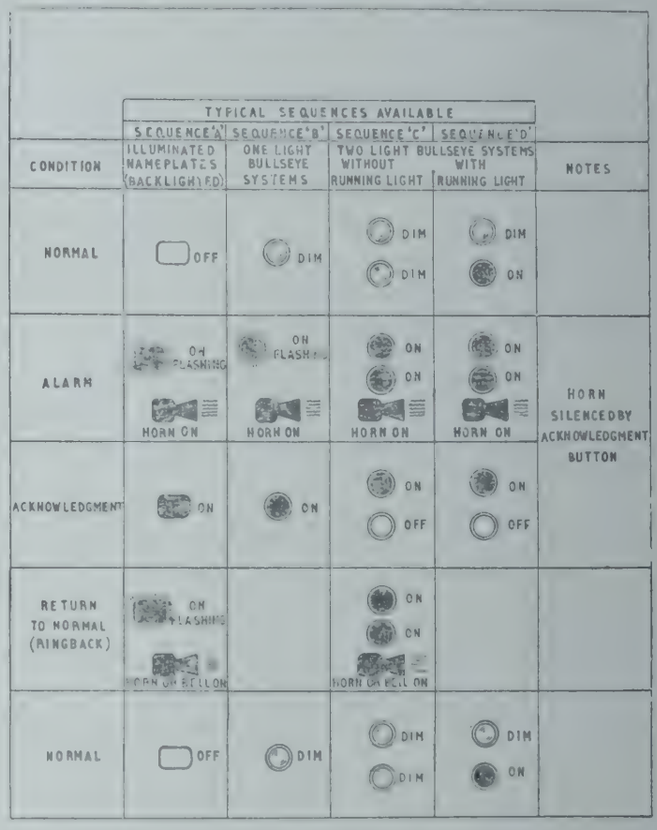

Fig. 1.—*Typical presentation sequences for alarm conditions*

The visual presentation of the alarm can either be in the form of individual signal lamps, colour identified where necessary for normal and abnormal conditions and titled by means of nameplates or an annunciator system where translucent nameplates are provided either individually or in banks, illuminated from the rear by the signal lamps. In either case they must be of adequate brightness in the face of normal illumination of the control room and preferably possess a wide angle of visibility. As an additional aid to attract attention flashing lights may be used and it is common for these to be arranged so that on first initiation the alarm light flashes and the audible warning sounds but on cancellation of the audible warning the flashing light reverts to a steady bright condition.

The use of multiple-light systems has many advantages. Two light systems are used for " normal and alarm " or for " high-low " while three light systems can give " high-normal-low " indications from one lamp at a time and two additional indications " below normal " and " above normal " with simultaneous illumination of two lights " normal and high " or " normal and low ". In some alarm sequences a " ring-back " system is provided which restores the audible alarm and the flashing when the alarm contacts revert to their normal condition. A further acknowledgment resets the system for further operation. In general, discharge lamps do not have a sufficient intensity for this duty and filament lamps must be used. These have a finite life for continuous burning (approximately 10 lamps per year at rated voltage will be necessary). This means that adequate provision must be made for indication of lamp failure. They may be continuously operated at low voltage showing a dim illumination level which can readily be discriminated from the bright alarm

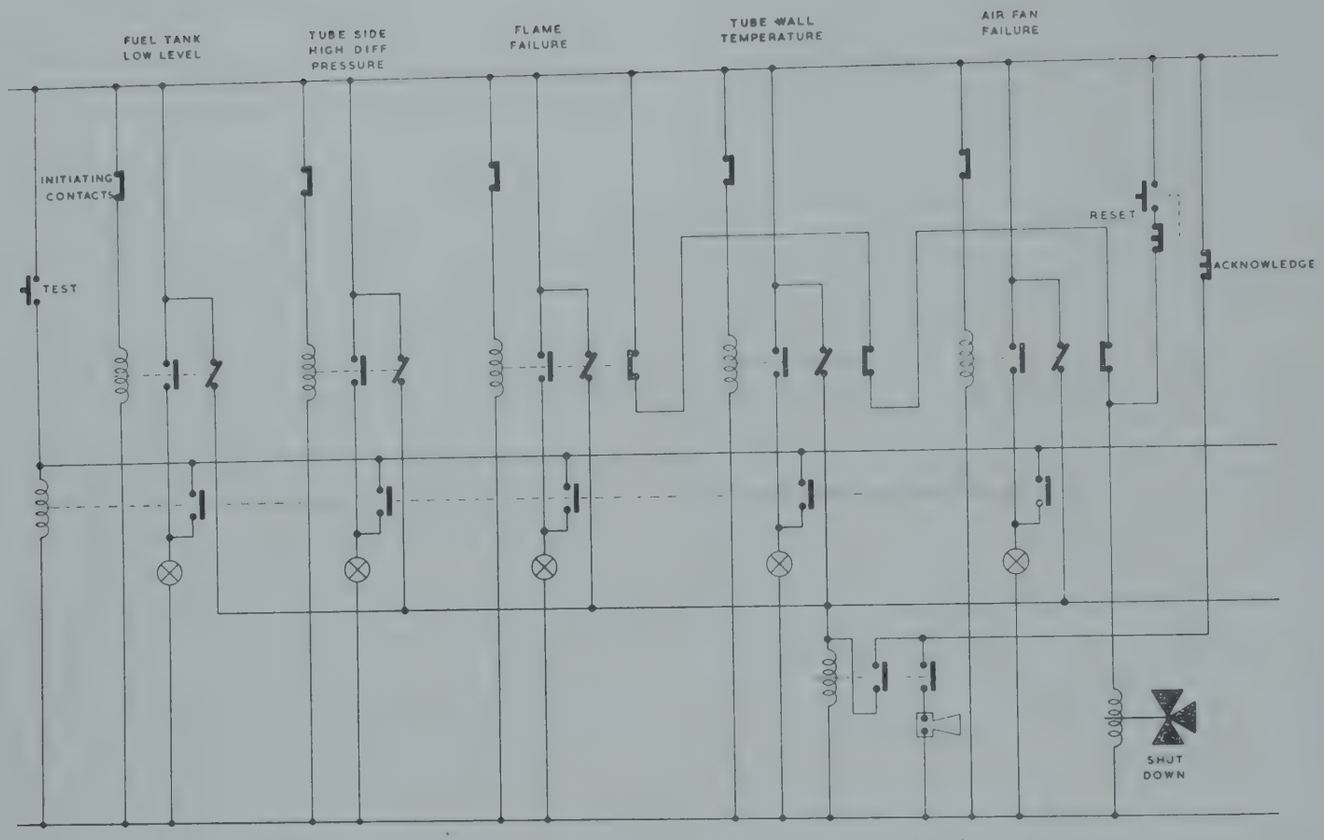

Fig. 2—*Typical wiring schematic for alarm system with shut-down circuit*

condition. Alternatively a test button may be installed, usually common to all alarms on the panel, which actuates all audible and visual alarms. This is checked once per shift and gives operators a desirable measure of confidence in the alarm system.

Complex alarm systems

By provision of appropriate contacts in the relay system several alarm points on a plant can be interlocked in such a way that any one of them by series connection will serve to shut down the plant. Such an arrangement is illustrated in Fig. 2. Such systems have an important part to play in the safe operation of the plant but very careful consideration should be given before a high degree of automatic shut-down is introduced. The cost or danger of a shut-down may well exceed the immediate hazards of continuing operation. In addition, after a plant is shut down automatically it is frequently difficult to identify which of the particular interlocked variables was responsible. In the safety systems applied to nuclear power reactors, for example, the consequences of shut-down are so serious that a " two out of three " safety system is used. This means that three independent installations are made at all alarm points. Before shut-down occurs two out of the three must indicate alarm conditions. This is a safeguard against failure of the alarm devices themselves. This technique will not normally be justified but it does emphasize the advantages of simplicity in design and reliability in operation required in alarm systems. Many automatic shut-down systems require manual restarting. In the simplest case, for example, flame-failure alarm will shut off the fuel and it cannot be restarted until some suitable interlock system has been actuated by the operator. This permits the necessary purging of the furnace chamber and ignition of pilot flames. The interlock and shut-down operation may be electric using solenoid valves or pneumatic using small air pilot valves.

Where complex shut-down systems are employed the reliability of power supply is most important and independent emergency electrical systems are often used. Low voltage d.c. supply with storage battery support has many advantages. The location of fuses and isolators in such systems is most important since a momentary overload in one of the safety circuits can blow a fuse and shut the whole plant down.

Conclusions

The large majority of instruments applied in process operation and control make a contribution to the safety of operation of the plant. Facilities for remote data transmission and automatic process control reduce even further the hazards of operating plants that would otherwise be substantially impossible to run in a safe condition. A range of safety and alarm systems has been developed which serve to limit the consequences of the inevitable failures and major disturbances that will occur on any plant and which, in the absence of adequate warning and perhaps automatic shut-down of the process, would cause very serious results.

Acknowledgment

Acknowledgment is due to L. S. Yoxall, Esq., Managing Director, Foxboro-Yoxall Limited, for permission to present this paper.

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DISCUSSION OF PAPERS PRESENTED AT THE FIRST SESSION

Mr. R. J. KINGSLEY asked how the Factory Inspectorate communicated its developing thought to practising design engineers. It seemed to be extraordinarily difficult to ascertain what the Factory Inspectorate, as a body, was thinking. The Factories Acts were limited in scope and by no means covered the whole of the experience and judgment of the Department. It seemed desirable for the Inspectorate to publish recommendations from time to time, based on its very considerable experience of hazards in the chemical field. They need not take the form of legislation.

Dr. MATHESON replied that the Ministry issued a large number of publications in the form of pamphlets, booklets, etc., that dealt with questions of industrial safety. Some of them were concerned with fire and explosion and with health risks. It was realised that more were needed and it was intended that more should be issued, but their preparation took time and individual problems—many of them demanding immediate attention—were keeping the Chemical Inspectors busy. In the absence of published information on a problem, however, it was always possible to ask the District Inspector what information was available in the Inspectorate about the matter in question.

Mr. K. M. HILL said that Thackara *et al.* had considered the likelihood of the various hazards which might occur in different sections of plant, and had rated them accordingly. In specifying protective measures, however, they did not indicate whether, in assessing their likelihood and in applying suitable protective measures, they assumed a number of simultaneous failures. In atomic energy it was the practice to design for two simultaneous failures; more recently designs were on the basis of more or less three simultaneous failures before a hazard was created, and the implication of Thackara's paper was that one single failure, assumed and guarded against, was in itself sufficient.

Mr. THACKARA said that a little guidance was given in the paper, " Where practicable, all **A** hazards (very serious) and **B1** and **B2** (serious and possible) and **C1** (less serious but likely) are positively guarded against, others are not." The approach examined the consequences of several simultaneous failures. If the results of such a series of failures were held to be very severe precautions would be taken.

Mr. HILL said that he assumed that " positively guarding against " referred to one single measure.

Mr. THACKARA said that if it was possible to guard against a serious consequence of failure by a protective measure achieved either by change in design which eliminated the source, or by a protective device, they would guard against it. The illustrations were a guide and one built up, over a long period, some better yardstick for applying judgment.

Several measure in combination might be used. A simple example was where rate of temperature rise actuators shut down a fan, doused the system with carbon dioxide and water, closed dampers, etc.

Mr. F. E. REUILL also referred to the paper by Thakara *et al.* where it was stated " . . . mixing of two materials giving rise to a high rate of liberation of heat (*e.g.* sodium and water) ".

Mr. Reuill asked if the authors had actually mixed those materials.

Mr. THACKARA replied that the process which gave rise to that example was sodium reduction in the manufacture of fatty alcohol. The process did not involve the addition of sodium to water. Precautions had to be taken against accidental contact.

Mr. H. A. ANSON asked if it was safe to repair, by welding, steel tanks which had been the subject of corrosive attack by mineral acids and what precautions had to be carried out to remove any residual hydrogen.

Mr. Anson wondered if there were any incidents on record which might be attributed to the presence of residual hydrogen in the structure of the metal.

Dr. MATHESON said that such a vessel could be repaired safely by welding, but stringent precautions would have to be taken in purging the vessel to ensure that hydrogen was removed from every corner and cranny. If further precautions were considered necessary the vessel could be charged with inert gas, or a continuous and copious current of air could be maintained through the vessel to prevent residual traces of hydrogen from forming local flammable concentrations.

There were no recorded incidents of explosions during the repair of such tanks.

Mr. J. A. ROBINS said that Dr. Matheson had mentioned a number of instances of explosions of carbonaceous dust. Could he say whether there were any known cases of explosions due to coal dust in conveyors, for instance, between coal stocks and overhead storage in a power station.

Dr. MATHESON replied that there were not any examples in actual coal conveyance. Certainly, they had had a number of explosions with pulverised fuel. In his recollection, in the earlier days, such explosions were all associated with the cyclones to which the pulverised material was delivered before it was distributed by means of one conveyor to the bunkers in front of the boilers. In more recent times they had been associated with the combined mill and classifying system which had a capacity of a similar order to the cyclones which were used in the earlier days, and were considered to be associated with flash-back from the actual boiler, the pop

in the actual combustion chamber striking back and reaching its maximum violence in the classifying system. But, in the actual conveying system for coal as distinct from a pneumatic conveying system for pulverised fuel, he could not think of any.

Mr. G. V. Day asked if Dr. Matheson would comment on the approach and the standard adopted abroad, particularly on the continent, with regard to some of the hazards and problems he had discussed, and would he mention any differences or particular points.

Dr. Matheson replied that he had not had much opportunity to make a systematic comparison of foreign standards with those of the U.K. Sometimes it seemed that more reliance was placed abroad on personal protection in the form of overalls and respirators, while in this country first thought would be to provide precautions on the plant to prevent, as far as possible, the dangerous material from getting from the plant to the man. But that was merely a difference of emphasis—both forms of precaution were used generally.

He had noticed that America and Britain had kept pace with one another remarkably closely in developing standards to deal with risks associated with industrial explosions.

Mr. D. M. Elliott referred to bucket elevators which Dr. Matheson had mentioned on page 3 of his paper. What did Dr. Matheson term a safer type of elevator ?

Dr. Matheson replied that, in the bucket elevator there was an air space down which dust could and did drop from the throw-off point at the top thus giving rise to a dust cloud inside the elevator casing. Experience had shown that, at times, this dust-cloud was present in the form of a flammable concentration.

Certain elevators such as vertical worm elevators and some types of " en masse " elevators did not have a space in which an explosive dust-cloud could form. In addition there were elevators that raised dusts and powders in a fluidised condition. Those were the elevators that he had in mind when he referred to safe types of elevator.

Mr. K. M. Hill said, with regard to the use of instruments for safety protection, if one looked at the instrument maintenance record, one found one had 95% or 90% reliability of a particular instrument ; unless one was going to duplicate all instruments, how did one overcome the problem of probiding real safety from instruments which could not be relied upon all the time.

Mr. Isaac replied that he had attempted in the paper to stress the important factors in designing instrumentation systems to give a high degree of reliability. He agreed that if any particular installation gave a serviceability of only 90—95% it did not constitute a very positive safeguard. However, most modern instrument installations could give very much better performance. He stressed that simplicity and reliability were the main requirements and that demanded high quality engineering, equipment, and maintenance, which of course involved cost but nowhere on a plant was expenditure better justified.

Failure of instrument power supplies or similar eventualities could be guarded against by the use of " fail safe " systems.

Duplication of alarm equipment and the " 2 out of 3 " principle had been mentioned as the ultimate case. The latter was justified in the field of reactor protection in view of the fact that the complex nucleonic measuring circuits used were not as reliable in performance as, say, a simple thermometer.

The use of two independent and different systems for a single variable was common. For example, on oil pipe-lines pump suction and delivery pressures were the critical variables and these were normally measured by independent recorders and pressure gauges with the alarm from yet another independent pressure switch. For maximum safety independent pressure tappings are used.

In the paper, mention was made of vapour phase oxidation ratio alarms. In such cases it was usual to duplicate the whole measuring installation and the alarm devices for maximum protection.

Mr. P. Grantham asked Mr. Isaac if he had found any way of guarding against fuse failure.

Mr. Isaac replied that he felt that that was a most critical and practical point. Failure of fuses in alarm circuits was a potential hazard but if interlock shut-down operators were also involved the effect could be very serious as it would shut down the plant. Clearly the solution lay in careful attention to the electrical distribution circuitry allocating the critical circuits individual fuses and connecting them into the supply on mains fuses not normally subject to overload. Careful engineering was needed at an early stage in the layout to select the least vulnerable mains supply. The use of low voltage circuits (*e.g.* 24v) permitted working on an alarm system without isolating the supply.

Mr. V. Kenworthy said that he had always felt that if one could devise a practical checking system for instruments everyone would be very much happier. For example, when passing a sensitive element point on the plant, as one went past, one could press a button to simulate an effect, and test the whole system throughout, right back to the recorders or controllers.

Mr. Isaac replied that some measure of test facility not greatly different to that described was frequently available, *e.g.* test switches on multi-point temperature indicators. However, it was more normal to provide test features only on the alarm devices and relays to simulate the initiation device. That had been described. To go further than that the problem lay not so much in the production of the test signal as in the interpretation of its effect. That was more the concern of the skilled instrument mechanic.

It was common practice on plants with comprehensive safety-shut down systems to test them by using them to shut down the plant when it was necessary to cease operation for a period. That is, an alarm condition was deliberately produced and the plant allowed to shut down automatically. That provides the best and most practical test but, of course, only on infrequent occasions.

Mr. A. P. Oele asked if there was an essential difference between the fully electronic installation and the pneumatic system, from the standpoint of safety.

Mr. Isaac was reluctant to generalise since the answer might well be confused by considerations of the equipment's

mechanical performance. Assuming that to be equal the main difference was in the nature and reliability of the power supply. The storage capacity of the receivers in a pneumatic installation did allow several minutes' margin of safety in the event of power failure whereas any electric system would be seriously upset by only a few seconds interruption of power. Normally therefore, standby power supplies of some sort are necessary. Where electric/hydraulic valves were used they did not normally have one direction of failure if the signal failed. Air-operated valves, however, were spring-opposed and would normally open or close as required in the event of power failure.

In general, however, while each type had its own characteristic requirements from the safety standpoint, there was no reason why either should not provide a safe and reliable installation if the requirements were observed.

Mr. C. K. W. COLSON wrote :

Electrical equipment which carries a Buxton flame-proof certificate is not certified as safe in atmospheres of hydrogen. What equipment for lights and motors would Dr. Matheson recommend for use in a building where hydrogen might be present ?

On the writer's works there are pneumatically operated hammer-guns using beryllium-copper needles. Would Dr. Matheson say that it was safe to use them in buildings where inflammable vapours might be present ? They will not themselves cause a spark, but can a spark be caused by fast-flying chips of rust ?

Dr. MATHESON wrote in reply to Mr. Colson :

A pressurised system might be used for hydrogen. Controls for such a system to cut off the supply when the pressure falls are available commercially. In addition, complete pressurised systems are also commercially available. Otherwise the lighting would have to be installed outside the room in question, and the light transmitted through sealed windows.

These remarks also apply to motors. When, however, the motor is outside the room, it drives the plant by a shaft passing through a gas-tight gland in the separating wall.

PAPERS AND DISCUSSION AT THE SECOND SESSION

THE RELIEF OF PENTANE VAPOUR-AIR EXPLOSIONS IN VESSELS

By J. H. BURGOYNE, D.Sc., Ph.D., F.R.I.C.* and M. J. G. WILSON, Ph.D., A.R.I.C.*

SUMMARY

The explosion of pentane-air mixtures, initially at atmospheric pressure, in two cylindrical chambers of internal diameter 4 ft 2 in. and length-to-diameter ratios approximately 1 : 1 and 3 : 1 has been studied. The vessels had capacities of 60 and 200 ft³ respectively.

Rates of pressure rise are greater than can be predicted on a basis of data for the laminar burning velocity, the difference being greatest for mixtures considerably richer than stoichiometric (2·56% pentane). The fastest pressure rise occurs with the mixture containing 3·5% pentane. The difference between observed and calculated rates may be attributed to the diffusional instability of the flame envelope and to other causes.

Rates of explosion are increased by distortion of the initially spherical flame envelope, either by mechanical stirring or by the outflow of gases through a relief opening in the vessel. In consequence, the effect of a relief area in lowering the peak pressure is less than would be expected.

The bursting of a diaphragm covering the relief opening also causes acceleration of combustion. A closure consisting of a smoothly-opening plate-valve avoids this effect and gives a peak pressure little, if any, greater than that which occurs in the absence of any closure.

For the two vessels examined, the relief area necessary to give a certain peak pressure appears to be a function of the least cross-sectional areas of the vessels (which are the same) rather than of their volumes or total surface areas. However for mixtures whose rate of explosion is influenced to varying degrees in different vessels by combustion wave instability or other disturbances, such relations are bound to be obscured.

Introduction

It is possible, in principle, to control the pressure to which a vessel is subjected by a gas or vapour explosion occurring within it by the provision of areas of relief through which the explosion gases can be released. In making such provision, knowledge is required of the area of relief necessary in relation to the size and strength of the vessel and of the manner in which the relief opening is to be covered for normal working.

The theoretical treatment of the subject presents a number of difficulties, and in the present state of knowledge it is not possible to calculate relief requirements from first principles. Even the relatively easier problem of scaling the results of practical measurements contains some pitfalls. In these circumstances, empirical information has considerable value, although to be of the widest possible use it should be so obtained as to give information either on the scaling problem or on the prospect of theoretical computation, or both.

The measurements recorded in this paper were made for a practical purpose, but are perhaps of wider interest in that they are in a corner of the field that has hitherto been not much explored. The explosion volumes, though compact, were fairly large (60 and 200 ft³) and the relief areas used were small enough to give fairly high explosion pressures. The explosive media employed consisted of pentane vapour-air mixtures of various strengths, the pressure and temperature prior to explosion being in all cases atmospheric.

Experimental Equipment

The explosion vessel used in the experimental work was an adapted marine boiler shell of internal diameter 4 ft 2 in., and 11 ft 6 in. long (excluding the curved ends). The total volume was about 200 ft³ but for many of the experiments approximately two-thirds of the volume was filled with tightly-packed sandbags and walled off with cement-faced brickwork from the remaining free space, which amounted to 60·6 ft³. An outline plan of the vessel is shown in Fig. 1.

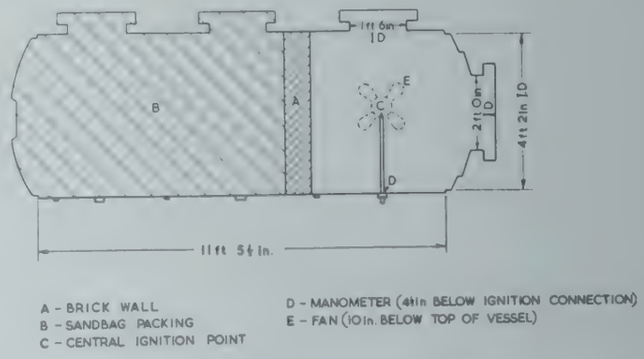

Fig. 1.—*Outline plan of explosion vessel*

For the purpose of these experiments the vessel had four large holes, three × 18 in. diameter along one side, and one × 24 in. at the end. These could be used as open vents, but each had a flange drilled and tapped so that orifice plates, relief closure devices, or blank flanges could be attached. Small holes for the introduction of pentane, for ventilation, for pressure measurement, and for ignition were provided opposite the 18 in. holes and the shell was tested hydraulically to 350 lb/in² after modification.

As indicated in Fig. 1, a fan was situated near the top of the 60 ft³ space. This was used for mixing and it could be run during an explosion to promote turbulence. It was operated by a 1420 r.p.m. constant-speed motor and the intensity of stirring could be varied by using blades of different lengths.

The manometers used were of types described elsewhere. They included two optical instruments developed by the U.S.

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Bureau of Mines and the Safety in Mines Research Board respectively. It was soon found, however, that explosions were being obtained which produced transient pressure effects and in order to obtain better records in these circumstances a piezo-electric manometer due to Margerson and Robinson[1] was adopted. Each manometer used was calibrated at intervals with a reservoir of compressed air adjusted to a series of known pressures.

In the earlier part of the work the source of ignition was a coil spark, though a condenser discharge was used for weak mixtures. Later, the method used was to discharge a 16 microfarad condenser at 360 volts through a short length of 0·1 mm aluminium wire. This proved a reliable source and gave consistent results. Photographs showed however that this source occasionally threw off small particles of aluminium which started separate flames, thus giving rise to multi-point ignition over a small volume.

Before each experiment, the vessel was thoroughly ventilated by means of an air blower. The predetermined amount of liquid pentane (in the range of 200–300 ml for the 60 ft³ space) was forced by nitrogen pressure through a spray nozzle into the vessel. The fan was run during injection of the hydrocarbon and for about one minute afterwards. The composition of the mixture produced was checked occasionally by analysis of a sample in a Bone and Wheeler apparatus. If an explosion vent was to be used it was covered with waxed paper, cellophane, or otherwise, before injection of the pentane.

Results

Pressure-time records were first obtained for the explosion of various pentane-air mixtures in the 60 ft³ space without any form of relief. With more than about 2·7% pentane, pressure oscillations developed and reasonably satisfactory records could only be obtained using the piezo-electric manometer. Records for the 2·7 and 3·5% pentane mixtures are compared in Fig. 2. In the latter case the oscillations that developed were initially of a smooth waveform, later becoming sharp-peaked. Such explosions produced a loud note, audible for about a second, having a frequency similar to that of the recorded oscillations, *i.e.* a little over 300 cycles per second. In Table I data from the pressure records are shown. These are derived from the mean pressure-time curves where oscillatory records were obtained.

The oscillations with rich mixtures were almost completely suppressed by running the fan during the explosion. Otherwise

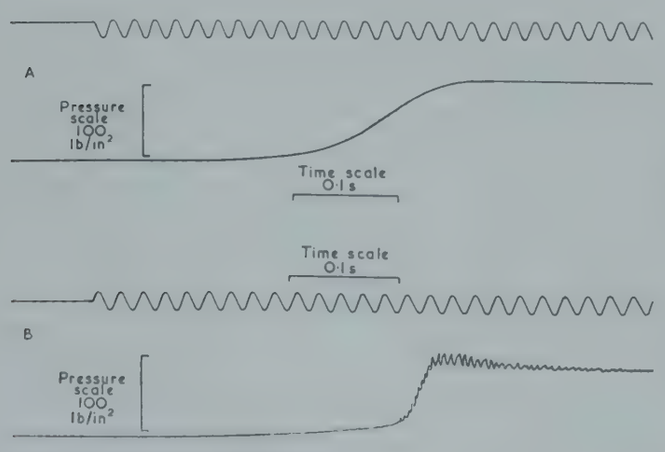


Fig. 2.—*Explosion pressure-time records for pentane-air mixtures in 60·6 ft³ vessel*
A 2·7% B 3·5% pentane

TABLE I.—*Explosions of Pentane-Air Mixtures in 60·6 ft³ Vessel with Central Ignition*

Mixture : pentane (%)	Maximum pressure (lb/in² g)	Maximum rate of pressure rise (lb/in² ms)	Time to maximum pressure (ms)
2·0	93	0·39	600
2·3	108	0·75	420
2·7	113	0·9	330
3·0	117	1·7	290
3·25	122	3·3	244
3·5	110	3·7	316
4·0	106	3·2	508
4·3	109	2·8	435

the form of the pressure record and the maximum pressure attained were unchanged by stirring, but, as is illustrated in Table II, the rate of pressure rise was increased in accordance with the fan size.

TABLE II.—*Effect of Stirring on Explosion of 2·7% Pentane-air Mixture in Closed 60·6 ft³ Vessel*

Maximum pressure attained, about 113 lb/in² g in each case.
Fan speed : 1420 r.p.m.

Fan diameter (in.)	Maximum rate of pressure rise (lb/in²ms)	Time to maximum pressure (ms)
None	1·1	340
12	2·1	135
17·5	3·95	95
24	5·75	75

Characteristics of pressure records obtained with a series of pentane-air mixtures while using a paper-covered 12 in. diameter relief area are shown in Table III. In this series, pressure oscillations became pronounced between 2·4 and 2·5% pentane and combustion, was markedly accelerated, resulting, with the presence of the vent, in a sharp rise in the maximum pressure recorded. As with the unvented vessel however, the maximum rate of explosion was observed with the 3·5% pentane mixture.

TABLE III.—*Explosion of Pentane-air Mixtures in 60·6 ft³ Chamber with 12 in. diameter Paper-covered Vent*

Mixture : pentane (%)	Maximum pressure (lb/in² g)	Time to maximum pressure (ms)
2·4	7	735
2·45	11	576
2·5	35	382
2·7	43	289
3·5	56	249
4·0	53	347

Table IV shows the effect of (paper-covered) vent diameter and of stirring with fans of various sizes upon the maximum explosion pressure observed with a 2·7% pentane-air mixture. Records for the unstirred mixtures with 6, 12, and 18 in. vents are shown in Fig. 3. These show, in addition to the pressure-time curve, a 50-cycle timing wave up to the moment of ignition, followed by the signal from a photocell pointing across the vent. Oscillations become more marked with increase in vent size and in mixture strength. Stirring reduced oscillation somewhat (see Fig. 4), but although it accelerated combustion in most cases, the effect on the maximum explosion pressure in the presence of vents was not large and with the 18 in. vent the maximum pressure was actually reduced by stirring at the lower rates.

TABLE IV.—*Effects of Diameter of Paper-covered Vent and of Stirring on Maximum explosion Pressure for 2·7% Pentane-air Mixture. Fan Speed 1420 r.p.m.*

Vent diameter (in.)	Fan diameter (in.) None	12	18	24
	Maximum explosion pressures (lb/in² g)			
None	113	113	113	113
6	73	80	—	—
12	43	45	47	65
18	22	9	18	33
24	4	—	—	12

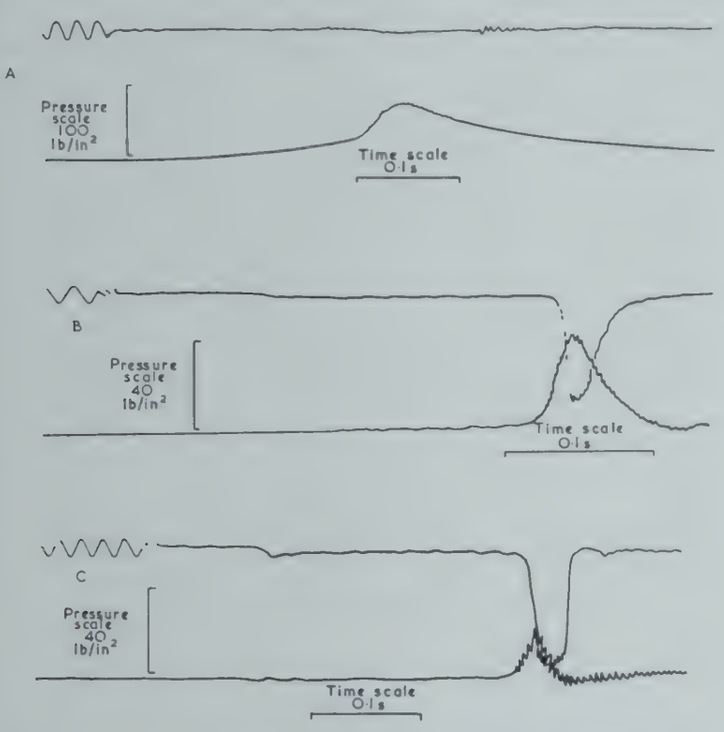


Fig. 3.—*Explosion pressure-time records for 2·7% pentane-air mixture in 60·6 ft³ vessel, with circular (paper-covered) vents of diameter:*
A 6 in. B 12 in. C 18 in.

The upper trace, after ignition, is that of the signal from a photocell viewing the emergence of flame from the vent.

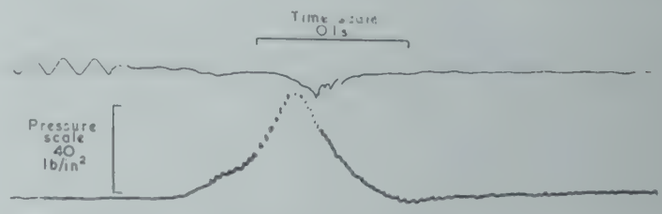


Fig. 4.—*Explosion pressure-time record for 2·7% pentane-air mixture in 60·6 ft³ vessel, with 12 in. diameter (paper-covered) vent, stirred by 12 in. fan at 1420 r.p.m.*

The upper trace, after ignition, is that of the signal from a photocell viewing the emergence of flame from the vent.

In the experiments with vents so far described, the opening was covered with waxed brown paper which burst at about 0·5 lb/in². It appeared from a study of the records that the bursting of this cover was itself tending to cause oscillation and this effect was further studied by substituting different forms of vent cover. Results are summarised in Table V. Bursting or opening pressures were read from the pressure records and were not determined independently. Although with the 2·7% pentane mixture reduction of the bursting pressure of the cover resulted in substantially slower explosions and lower maximum pressures, no such effect was apparent with the faster-burning 3·5% mixture.

Table VI shows results obtained with an 18 in. diameter spring-loaded plate valve having a plate thickness of 1 in. Fig. 5 shows the pressure records for the 2·7 and 3·5% pentane mixtures. Also included on the same time base are records of the lift of the valve plate. The pressure required to open the valve against the spring loading was 4 lb/in² but higher opening pressures were sometimes observed, due presumably to sticking and friction, although these were eliminated as far as possible. The travel of the plate was limited by a rubber buffer to about 3 in. and the maximum cylindrical relief area was about 170 in² as compared with 255 in² for

TABLE VI.—*Pressures Obtained in Pentane-air Explosions in 60·6 ft³ Vessel with 18 in. Vent Closed by Plate-Valve Opening at 4 lb/in² g*

Mixture: pentane (%)	Maximum pressure (lb/in² g)
2·0	10
2·7	23
3·5	33

TABLE V.—*Effect of Method of Closure on Relief of Pentane-air Explosions in 60·6 ft³ Vessel. Central ignition*

Vent diameter (in.)	Cover: Material	Cover: Opening pressure (lb/in² g)	2·7% mixture: Maximum pressure (lb/in² g)	2·7% mixture: Time to maximum pressure (ms)	3·5% mixture: Maximum pressure (lb/in² g)	3·5% mixture: Time to maximum pressure (ms)
12	Card (1)	Negligible	25	377	58	192
	Card (2)	0·2	41	265	—	—
	Paper	0·5	43	289	56	249
18	Card (1)	Negligible	8	396	30	260
	Card (2)	0·2	21	348	—	—
	Paper	0·5	22	375	32	286
	Cellophane (slit before firing)	0·5	14	367	—	—
	Cellophane	2·4	29	215	—	—
	Cellophane (three layers)	6·2	29	241	—	—

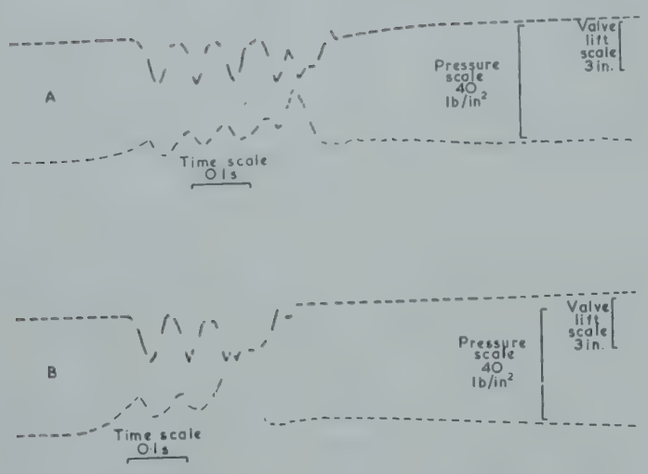


Fig. 5.—*Explosion pressure-time records for pentane-air mixtures in 60·6 ft³ vessel with 18 in. diameter relief valve:*
A 2·7% B 3·5% pentane

the 18 in. diameter opening. In spite of this, and of the relatively high opening pressure, the maximum pressures recorded were not significantly greater than with the paper-covered 18 in. vent. With a ¼ in. thick valve-plate and an opening pressure of 1·15 lb/in² the maximum pressure with a 2·3% pentane mixture was only 7 lb/in². Stirring with the 12 in. diameter fan at 1420 r.p.m. had little effect on the explosion pressure with such a relief valve.

It will be seen from Fig. 5 that the valve plate " bounces " during the explosion, with the consequence that there is a low frequency oscillation of the pressure. With the faster-burning mixtures the greatest pressure is reached on the last oscillation, whereas with weak mixtures it is the first pressure oscillation which has the greatest amplitude. The higher frequency oscillation noted in the closed vessel and with paper-covered vents was scarcely observable when relief valves were used.

Experiments using the full capacity of the explosion chamber were confined to those mixtures which in the 60 ft³ section had given the fastest explosions. The results with the vessel entirely closed are shown in Table VII, from which it may be seen that, although the maximum pressures are much the same as in the smaller vessel, the rate of pressure rise is substantially reduced, *i.e.* the explosion is of longer duration. In the larger vessel, the pressure oscillations were less marked than in the smaller chamber.

TABLE VII.—*Explosions of Pentane-air Mixtures in 200 ft³ Vessel*

Mixture : pentane (%)	Maximum pressure (lb/in² g)	Maximum rate of pressure rise (lb/in² ms)	Time to maximum pressure (ms)
3·0	112	0·8	505
3·5	111	1·26	440

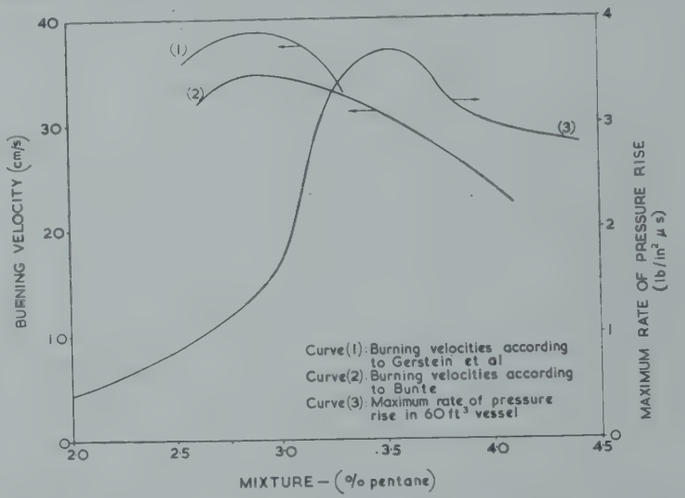
The effects of the following vent arrangements in the 200 ft³ vessel were investigated :—

(i) One 18-in. vent in the mid-position along the side of the vessel.
(ii) One 24-in. vent in the end of the vessel.
(iii) Three 18-in. vents along the side of the vessel.

With the 18-in. side vents in use, the igniting source was placed in the centre of the vessel. With the 24-in. end vent, the source was on the axis of the cylinder but alternatively at the ends near to and remote from the vent. In all cases the vent openings were covered with light cards. The results obtained are summaried in Table VIII.

Discussion and Conclusions

In Fig. 6, laminar burning velocity data for pentane-air mixtures, derived from the literature, [2,3] are compared with maximum rates of pressure rise measured (for the 60·6 ft³ chamber) in the present work. Whereas the maximum burning velocity is observed with a 2·9% pentane mixture, the 3·5% pentane mixture gives the greatest rate of pressure rise.


BURNING VELOCITY (cm/s)
MAXIMUM RATE OF PRESSURE RISE (lb/in² μ s)
MIXTURE – (% pentane)
(1)
(2)
(3)
Curve(1): Burning velocities according to Gerstein et al
Curve(2): Burning velocities according to Bunte
Curve(3): Maximum rate of pressure rise in 60 ft³ vessel

NOTE. The units along the right hand vertical axis should be milliseconds not microseconds as indicated.

Fig. 6.—*Comparison of burning velocities and maximum rates of pressure rise on explosion in 60·6 ft³ vessel for pentane-air mixtures*

It is possible to calculate the pressure development that can occur in a spherical vessel of given volume due to the central ignition of a gas mixture having known burning velocity characteristics. This has been done for a 2·7% pentane mixture for a sphere of 60·6 ft³ capacity on the basis of values of the laminar burning velocity. The calculated pressure rise is, except perhaps in the early stages, considerably slower than was in fact observed with the same mixture in the 60·6 ft³ chamber. The difference is greater than can be accounted for by the approximations involved.

It appears that for explosion in the 60·6 ft³ closed vessel, with mixtures containing greater than stoichiometric propor-

TABLE VIII.—*Effect of Vents (card-covered) on Explosion of Pentane-air Mixtures in 200 ft³ Vessel*

Vents			Mixture : pentane (%)	Maximum pressure (lb/in² g)	Time to maximum pressure (ms)
Number	Position	Diameter (in.)			
1	Mid-side	18	3·25	22	655
1	Mid-side	18	3·75	35	760
1	End (ignition near)	24	3·5	4	680
1	End (ignition remote)	24	3·5	16·5	315
3	Along side	18	3·5	2·5–3·0	540–585
3	Along side	18	4·0	1·5–4·0	510–590

tions of pentane, there is some form of departure from laminar burning after the initial stage of the explosion, and that this is marked by the appearance of gas pressure oscillations in the record and of a corresponding audible note. Similar observations were made by Maxwell and Wheeler[4], but with their smaller explosion vessel (6 in. diameter, 15 in. long) the oscillatory phase of the explosion appeared only with a more restricted range of mixtures. The most marked effect, however, appeared, as in the present work, with about 3·5% pentane in the mixture.

Instability of the combustion wave is no new phenomenon. The vibratory stage, accompanied by increase of flame speed, has long been a recognised feature of flame propagation in tubes. Instability of propagation in flowing gases has aroused some interest in recent years, as has the question of the transition from deflagration to detonation during spherical flame propagation.

To discuss the matter in detail would be out of place in the present paper. Some aspects have been reviewed by Markstein.[5] It can be said however that various influences appear to be involved and that their relative importance depends upon the circumstances of flame propagation.

Since, with hydrocarbon fuels, instability is most noticeable, as in the present work, with fuel-rich mixtures, explanations based upon relative rates of diffusion of fuel and oxygen through the flame front have found favour.[5] A part may also be played however by natural oscillation of the burning gas of the column, by vibration of the containing vessel and auxiliary equipment, by the onset of turbulent flow conditions in the unburnt gas ahead of the flame,[6] and by the interaction of shock waves with the flame front.[7]

A spherical flame envelope represents the minimum surface enclosing a given volume of products and hence a minimum rate of burning at a given stage. Any disturbance of this spherical form, whether it consist of roughening due to turbulence, cell formation due to differential diffusion, or gross distortion due to external influences, will result in an increase in flame-front area and hence in an increase in the rate of burning. Gross distortion occurs when the mixture is stirred and hence there is an increase in the rate of burning which may be taken as a measure of the increase in area of the flame envelope brought about by the degree of stirring employed. (See Table II.) At the same time, the tendency to combustion instability is diminished, as Maxwell and Wheeler also observed.[4]

In a somewhat similar manner, the presence of a relief area will distort the flame envelope as the result of gas flow towards the vent. Thus, after the relief has opened, but before any substantial quantity of burnt gas has escaped, the rate of combustion may exceed the rate at the same stage in the closed vessel. This is actually observed and with small vent-areas the rate of pressure rise may exceed, for a time, the maximum rate occurring without any vent at all. The effect is more noticeable with the vent remote from the source of ignition than near to it, for in the former case the flame envelope whilst still remaining inside the vessel becomes more distorted due to outflow of unburnt gases. Hence a vent near the source of ignition is more effective in lowering the peak pressure than one at a distance from it. (Table VIII.) With a flame envelope distorted due to a vent, mechanical stirring of the burning mixture has relatively less effect.

So far as the closure of the relief vent is concerned, an increase in the opening pressure, by increasing the amount of combustion that has occurred before relief begins, generally increases the peak pressure finally attained. A closure, such as a diaphragm, which bursts suddenly at the opening pressure, appears to have its own disturbing effect upon the flame envelope, leading to acceleration of combustion. Therefore a closure that opens smoothly at a certain pressure, such as a plate valve, gives rise to a lower peak pressure than does a diaphragm which bursts at the same opening pressure. With rich mixtures, in which the flame envelope is disturbed in any case, this effect is not noticeable.

Explosion-relief areas have commonly been stated in relation to the volume they protect. This practice is unsatisfactory dimensionally, and it seems more rational to relate the relief area to some area function of the vessel itself. In the present instance two cylindrical chambers differing only in length by a factor of three, have been employed. For comparison of venting effects in the two chambers, the results with the 3·5% pentane-air mixture are most free from ambiguity, since they are least susceptible to effects due to the method of closure and to other disturbances. From an examination of these results (Tables IV, V, VI, and VIII) it is clear that equal relief areas are associated with substantially similar peak-explosion pressures in the two vessels. It appears therefore that the effect of the relief area in limiting the explosion pressure in vessels in the form of short cylinders (length/diameter less than 3) depends not upon the volume or surface area of the vessels but upon their cross-sectional area, which is the same for the two vessels used. The present results (though limited in number) indicate, in fact, that a linear relation exists between the peak explosion pressure and the logarithm of the relief area over most of the range of peak pressures. This suggests that for short cylindrical vessels differing in diameter a similar linear relation may exist between the peak pressure (P_{max}) and the logarithm of the ratio : cross-sectional area of vessel (A)/relief area (a). In this form, the results for the 3·5% pentane-air mixture may be related by :

$$P_{max} = 68{\cdot}0 \log_{10} A/a - 28{\cdot}6 \text{ (lb/in}^2\text{)}$$

for values of P_{max} from 5 to 100 lb/in^2.

Such a relation cannot of course hold for very low pressures or for those near to closed-vessel values.

Acknowledgments

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THE EXPLOSIVE DECOMPOSITION OF ETHYLENE OXIDE VAPOUR UNDER PRESSURE

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SUMMARY

To assess the hazards involved in the handling of ethylene oxide vapour in plant where a source of ignition may exist, an investigation has been made of the explosive decomposition of this material at 125°C and pressures up to 155 lb/in² abs and its mechanism considered. The igniting source employed consisted of a length of 31 s.w.g. Nichrome wire which was fused electrically. It is shown that the explosion is capable of suppression by inert diluents and the use of nitrogen in this connection has been particularly investigated. Less detailed observations have been made with ethylene, propane and butane as diluents. It was found that propylene oxide did not undergo explosive decomposition at 125°C and pressures up to 165 lb/in² abs.

Introduction

Ethylene oxide first assumed some commercial importance as a fumigant for the control of insect pests in foodstuffs. During the last twenty years, however, its widespread use as a chemical intermediate in the production of ethylene glycol and ethylene glycol derivatives has raised its status to that of a " heavy organic chemical ". The rapid expansion in its use in the U.S.A. may be judged by an increase in the estimated consumption from 108 million pounds in 1939 to 354 million pounds in 1949;[1] during the last decade, estimated production has jumped to 1300 million pounds.[2] By the end of 1960 it is estimated that production capacity in the United Kingdom will exceed 100 million pounds. If ethylene oxide is put to the same uses as in 1957, then 40% of the total production will be required for the manufacture of ethylene glycol ; the processing of solvents for the paint industry will account for 20% and that of liquid synthetic detergents for a further 15%.

At atmospheric pressure all mixtures of ethylene oxide in air containing more than 3% ethylene oxide are capable of being ignited. Following the occurrence of several explosions during fumigations, consideration was given some years ago to reducing the flammability of ethylene oxide in air. Early studies of its physiological properties had shown that its pesticidal effect is promoted by the presence of carbon dioxide which increases the respiration rate of the insect. For this reason, it was the custom to introduce 10% carbon dioxide into commercial ethylene oxide for use as a fumigant, a practice which also raised the vapour pressure to a convenient level for discharge from the cylinder. It is not surprising, therefore, that carbon dioxide was early considered for the purpose of suppressing the flammability of ethylene oxide. Jones and Kennedy[8] determined the effect of carbon dioxide on the limits of its flammability in air ; their results were later confirmed by other investigators[9, 10] using different experimental conditions. All possible mixtures of ethylene oxide in air can be made non-flammable at atmospheric temperature and pressure by adding at least 7·15 volumes of carbon dioxide to each volume of ethylene oxide present.[11]

In the absence of air, ethylene oxide is capable of exothermic decomposition and it has seen some use as a monopropellant in rocket motors. The liquid is stable when pure[4, 5] but at atmospheric temperature an exothermic polycondensation reaction in the liquid phase may be catalysed by impurities such as caustic soda.[6] The heat released during this process may cause the vapour pressure of the unreacted material to exceed the bursting pressure of a closed vessel.

The spontaneous decomposition temperature of pure ethylene oxide vapour at atmospheric pressure is reported[12] to be 571°C and it has been shown[7] that if a local source of ignition, such as a hot wire, is applied to ethylene oxide vapour, a decomposition reaction, accompanied by flame, may propagate from it and throughout the vapour if the latter is at a pressure greater than approximately atmospheric. The precise pressure limit for flame propagation which is observed depends upon the energy of the igniting source and the conditions of confinement.

The use of inert diluents to suppress the explosive decomposition of ethylene oxide in the absence of air was first investigated by Hess and Tilton.[12] There is some doubt as to the exact conditions of temperature and pressure under which they carried out their investigation but it is thought that they worked with a constant partial pressure of ethylene oxide of 45 lb/in² abs at a temperature of 40–45°C. In presenting their results, however, they assumed that the percentages of inert diluents needed to suppress the explosive decomposition of ethylene oxide vapour at partial pressures of 15–75 lb/in² abs and temperatures from 10–60°C were constant.

The increasing industrial use of ethylene oxide at higher temperatures and pressures has necessitated an investigation of the effect of these conditions on the amount of diluent needed to suppress explosive decomposition. In this connection the use of nitrogen has been investigated in some detail because it is readily available in large quantities. Less detailed observations have been made on the hydrocarbons, ethylene, propane, and butane.

Experimental

Apparatus

The explosion vessel used in this investigation, shown diagrammatically in Fig. 1, had an internal diameter of 4·5 in. and an internal volume of 148·9 in³. It was designed for a maximum dynamic pressure of 1500 lb/in² g. To reduce any tendency towards catalytic decomposition of the ethylene

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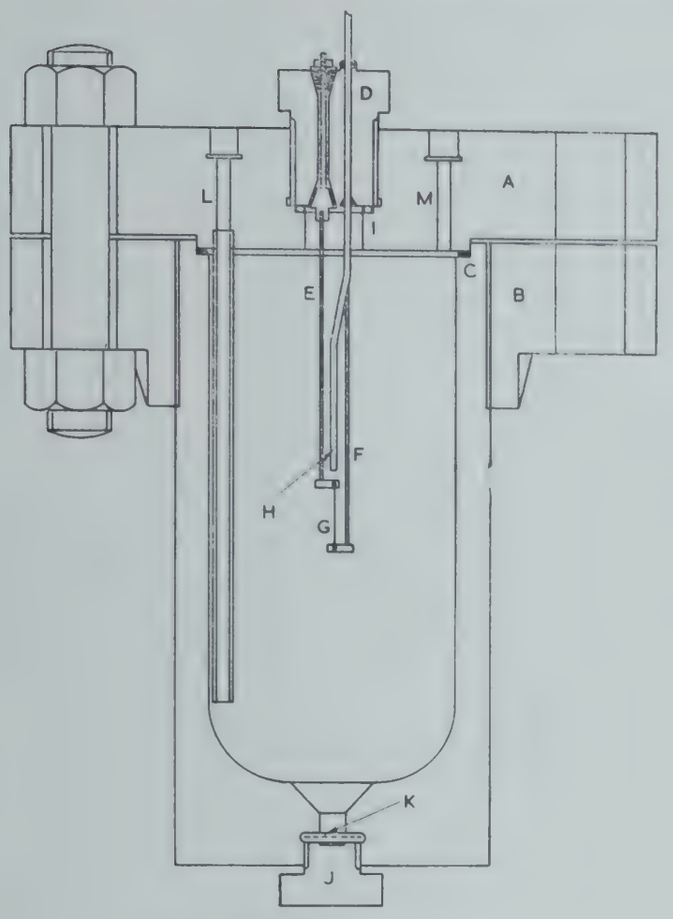


Fig. 1.—*Experimental pressure vessel*

oxide vapour on the walls, all those parts of the vessel coming into contact with the vapour were made of austenitic stainless steel (En specification 58B). No copper, silver, or other acetylide-forming metals were used in the construction of the vessel and its ancillary equipment in order to prevent the possible formation of acetylides which, if detonated, could have initiated prematurely the explosive decomposition of ethylene oxide.

The end cover, A, was attached to the screwed flange, B, by eight high-tensile steel nuts and bolts ; a semi-confined flat gasket, C, machined from fully annealed nickel, formed the seal between the cover and the end of the vessel. The firing plug, D, was provided with two electrodes, one of which, E, was electrically insulated from the plug by two cone-shaped Fluon bushes, while the other, F, served as an earth return. The ignition source, G, which consisted of a straight piece of 31 s.w.g. Nichrome wire 0·8 in. long clamped between the electrodes, was located near the centre of the vessel ; the end of a stainless steel sheathed thermocouple, H, which was welded into the firing plug was located near the ignition source. A hollow pressure-filled nickel joint ring, I, was used to obturate the firing plug so that the pressure-tight seal could be remade frequently without the use of excessive force. Provision was made to evacuate and fill the vessel through the two pipe inlets, M and L, the latter being provided with a pipe extension inside the vessel designed to promote mixing when an inert gas was added to the ethylene oxide.

The dynamic pressure measurements were made using two condenser-type pressure gauges, J. These gauges, one of which had a pressure range of 0–600 lb/in² g, and the other 0–1500 lb/in² g, were provided with flush, stainless steel diaphragms. The gauge in use was accommodated in a screwed recess at the end of the vessel, the seal being made on a nickel washer located between the body of the gauge and the outside surface of the vessel.

When in use each gauge formed part of the tuned circuit of an oscillator ; the radio frequency signal resulting from a change in capacitance of the gauge was fed to a frequency modulated pre-amplifier the output voltage of which was directly proportional to the change in capacitance and hence directly proportional to the pressure change on the diaphragm of the gauge. The output signal from the pre-amplifier, after suitable amplification, was displayed on the main cathode ray tube of an oscillograph. Electrical pulses of 0·1 s duration produced by a time marker, consisting of a tuning fork controlled vibrator circuit, were applied to a small marker tube. A permanent pressure-time record of the explosion, such as that shown in Fig. 3, was obtained by photographing both cathode ray tubes simultaneously with a rotating drum camera. The mark A on the record shows the time at which the wire was caused to fuse.

Each gauge, when screwed into position in the explosion vessel and maintained at the required operating temperature, was statically calibrated over the whole of its working range. The calibration, using nitrogen as the pressure-transmitting fluid, was made against a Bourdon-tube testing gauge which had been previously calibrated against a dead-weight pressure tester. To obviate the tightening-in effect caused by the distortion of the body of the condenser gauge when it was screwed into the vessel against the sealing gasket, it was necessary to recalibrate the gauge each time it was reseated in the vessel. In order to reduce the error in the pressure measurement caused by the flame front impinging on the diaphragm the gauge was protected by a piece of 200 mesh stainless steel gauze, K (see Fig. 1) which was fixed 0·125 in. in front of the diaphragm.

The vessel was supported at the centre of an enclosed electrically-heated oven which could be adjusted and controlled at any temperature from 25–200°C. Provision was made for the firing plug and pressure gauge to be withdrawn and replaced in the vessel as required, without having to remove the oven. Four thermocouples fixed to various points on the vessel enabled the temperature distribution over the outside surface of the vessel to be measured. It was found that when thermal equilibrium had been established with the contents of the vessel at 125°C the difference between the temperature at any point on the outside surface of the vessel and that at the centre did not exceed ± 2°C.

Fig. 2 shows a flow diagram of the ancillary equipment used to charge the vessel with ethylene oxide vapour and inert diluent. As in the case of the explosion vessel the pipe lines, valves, and all those items of equipment which came into contact with the ethylene oxide vapour were made from austenitic stainless steel.

Liquid ethylene oxide was stored under its own vapour in the feed-vessel, A, which could be refilled through a screwed cap. This vessel, which had an internal volume of 23·5 in³, was designed to withstand a working pressure of 200 lb/in² g ; it was protected by a bursting disc, B, rated to rupture at 250 lb/in² g.

Procedure

The detailed procedure for filling the explosion vessel with a mixture of ethylene oxide and inert diluent of known composition depended on the total pressure required and the vapour pressure of the inert diluent in the storage container. The procedure described here was that applied to an inert

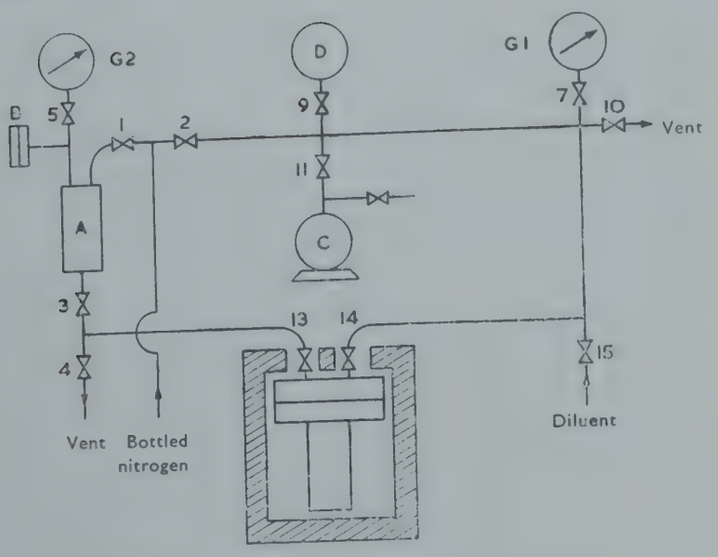


Fig. 2.—*Flow diagram of ancillary equipment used to charge vessel with ethylene oxide vapour and inert diluent*

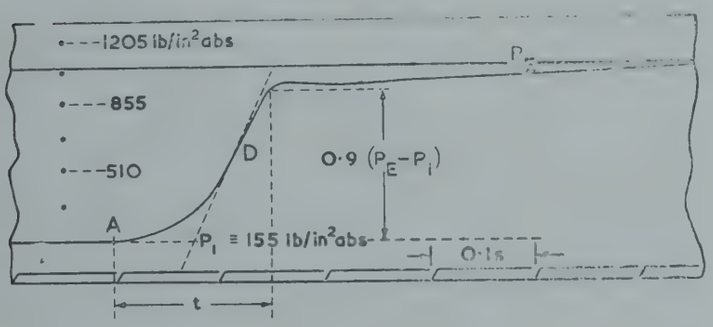


Fig. 3.—*Pressure-time record of the decomposition of ethylene oxide at an initial pressure of 155 lb/in² abs and temperature of 125°C*

diluent, such as ethylene, bottled in the form of a compressed gas.

After the explosion vessel had attained the correct temperature, usually 125°C, all valves except Nos. 7, 9, 11, 13, and 14 were closed and the vessel was evacuated using a rotary pump until the pressure recorded by the vacuum manometer, D, with valve 11 closed, was less than 1 mm mercury. Oxygen-free nitrogen was then admitted through valve 2 until a small pressure was registered by the compound Bourdon-tube gauge G.1 after which valve 2 was closed and the vessel re-evacuated. Valve 14 was then closed and valve 3 opened to allow ethylene oxide to be drawn slowly into the explosion vessel where it quickly vaporised until the vapour pressure in the explosion vessel was equal to that in the feed vessel. Oxygen-free nitrogen was then slowly admitted to the feed vessel via valve 1 and used to force more ethylene oxide into the explosion vessel until the required pressure of the ethylene oxide vapour as registered by the Bourdon tube gauge, G.2, had been attained. When equilibrium had been established valves 1 and 13 were closed and the remaining ethylene oxide in the feed bottle and pipe line was removed by a wet vacuum pump through valve 4. The inert diluent was admitted through valve 15, valves 9 and 11 being closed, until the pressure recorded by the compound Bourdon-tube gauge, G.1, was slightly less than the total pressure required in the explosion vessel. Valve 14 was opened and inert gas admitted to the vessel until the required total pressure was obtained. Valves 15 and 4 were then closed and the inert diluent in the pipe line was withdrawn through valve 10 using the wet vacuum pump.

After allowing about half an hour for the ethylene oxide and diluent to mix thoroughly the igniting wire was fused and the pressure-time trace photographed. When the products had cooled to 125°C the pressure in the vessel was measured using gauge G.1 after which the vessel was evacuated by the wet vacuum pump. In order to obtain consistent results for the dynamic pressure measurements it was found necessary to remove periodically the carbon deposited on the inside surface of the vessel as a result of the decomposition reaction.

Experimental Results

A preliminary series of experiments was made to ensure that the energy dissipated by the ignition source was adequate. No attempt was made in these experiments to measure the electrical energies dissipated; instead, Nichrome wires (80% Ni 20% Cr) of various diameters and each 0·8 in. long were caused to fuse by using an alternating current of 10A at 240 volts. In Fig. 4, the percentage of nitrogen by volume necessary to suppress the explosion of ethylene oxide at a partial pressure of 85 lb/in² abs and 125°C is shown as a function of the gauge and the cross-sectional area of the wire. It may be seen from this figure that provided the diameter of the Nichrome wire is greater than 34 s.w.g. the limit of explosibility of ethylene oxide in nitrogen is independent of the diameter to within the mean experimental error of the measurements (estimated to be ±1·5%). The source of ignition used for all subsequent experiments consisted of a straight piece of 31 s.w.g. Nichrome wire 0·8 in. long, the fusion temperature of which was taken as 1400°C.

Commercially available ethylene oxide and inert diluents were used without further purification; the sources of supply and the probable impurities are given in the Appendix.

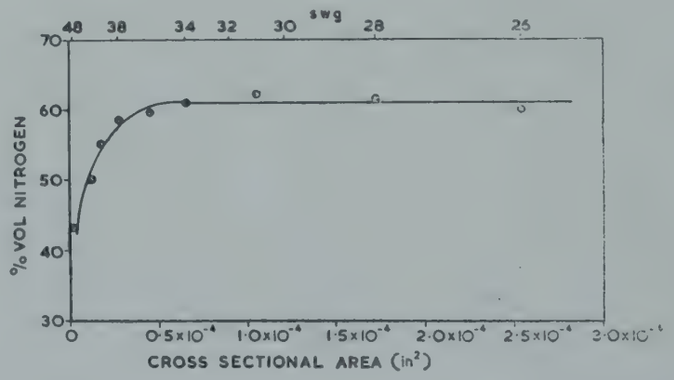


Fig. 4.—*Percentage of nitrogen necessary to suppress decomposition of ethylene oxide at a partial pressure of 85 lb/in² abs and at 125°C shown as a function of the cross-sectional area of the igniting wire*

Explosive decomposition of ethylene oxide vapour

The ratio of the maximum explosion pressure, P_E, to the initial pressure of ethylene oxide vapour, P_I, and the ratio of the final pressure of the products of combustion, P_F, to P_I are both plotted against P_I in Fig. 5. P_F and P_I were measured at 125°C and the ratios were calculated on the basis of the absolute pressures. Although the ratio P_E/P_I increases to about 6·4 when the initial pressure of ethylene oxide vapour is 155 lb/in² abs, the rate of the pressure rise was comparatively slow. Fig. 3 shows the pressure-time record for the explosion of pure ethylene oxide vapour at 155 lb/in²

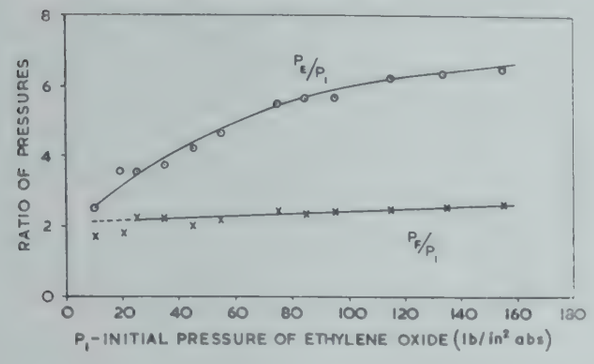


Fig. 5.—*The maximum explosion pressure, P_E, and the pressure of decomposition products, P_F, at 125°C as a function of the initial pressure of ethylene oxide, P_I, at 125°C*

abs. The maximum rate of increase of pressure $(dP/dt)_{max}$ which occurs at D is only $1{\cdot}2\times10^4$ lb/in² s. In Fig. 6, values of $(dP/dt)_{max}$ and the time taken, t, for the pressure to reach 90% of its maximum value are plotted against the initial pressure of ethylene oxide vapour.

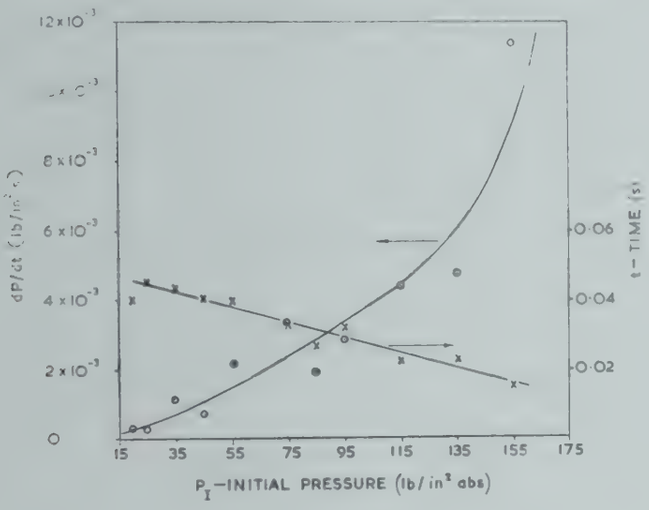


Fig. 6.—*The maximum rate of pressure increase, dP/dt, and the time taken to develop 90% of the maximum explosion pressure as a function of the initial pressure of ethylene oxide*

A chromatographic analysis of the gaseous decomposition products of ethylene oxide at initial pressures of 45 and 135 lb/in² abs was made using an apparatus incorporating a multicell thermal conductivity detector developed by Boreham and Marhoff.[14] The results of these analyses given in Table I show that at the higher pressure there is a marked reduction in the proportion of undecomposed ethylene oxide.

TABLE I.—*Analysis of the Gaseous Products of Combustion*

Composition of gas before ignition				
Partial pressure C_2H_4O (lb/in² abs) ..	45	135	85	85
Partial pressure N_2 (lb/in² abs) ..	—	—	16	55
Vol % N_2	—	—	16	39
Analysis of gaseous products (Vol %)				
H_2	15·1	16·1	15·3	7·2
CO	44·6	47·0	42·0	34·3
O_2	0·0	0·2	0·2	0·2
N_2	0·0	0·0	8·2	24·3
CH_4	29·6	35·3	29·9	27·3
C_2H_6	1·2	1·0	1·0	0·9
CO_2	0·2	0·3	0·2	0·3
C_2H_4	1·1	0·0	0·2	0·3
C_2H_4O (by difference)	8·2	0·1	3·0	5·2

The explosibility of propylene oxide

It appears from thermochemical considerations that propylene oxide is also capable of undergoing exothermic decomposition. It is possible, therefore, that at sufficiently high temperatures or pressures the vapour may become explosible on the application of a suitable source of ignition.

Using the same apparatus and procedure as for ethylene oxide, propylene oxide vapour at 125°C and at pressures up to 165 lb/in² abs was subjected to the standard ignition source (fusion of 31 s.w.g. Nichrome wire), but no sign of flame propagation as indicated by pressure rise was observed. It was concluded that propylene oxide vapour is not explosible at or below 165 lb/in² abs at 125°C.

Effect of inert diluents

In Fig. 7 the percentages by volume of nitrogen, ethylene propane, and butane necessary to suppress the explosive decomposition of ethylene oxide vapour at 125°C are plotted against the partial pressure of ethylene oxide in the gas mixture before ignition. These percentages were calculated on the assumption that all the gases obey the perfect gas laws over the range of pressure and temperature investigated.

It may be seen from this figure that whereas the percentage of diluent to suppress the explosibility of ethylene oxide increases with the partial pressure of the oxide vapour in nitrogen and in ethylene, in propane and butane the percentage appears to be constant over the limited range of pressures investigated. If 3% by volume of oxygen is added to the ethylene oxide vapour the requisite proportion of nitrogen at a partial pressure of ethylene oxide of 85 lb/in² abs is increased from 61·4 to 67·4%. Thus, had pure nitrogen been used for the experiments the values would have been only 0·3% lower.

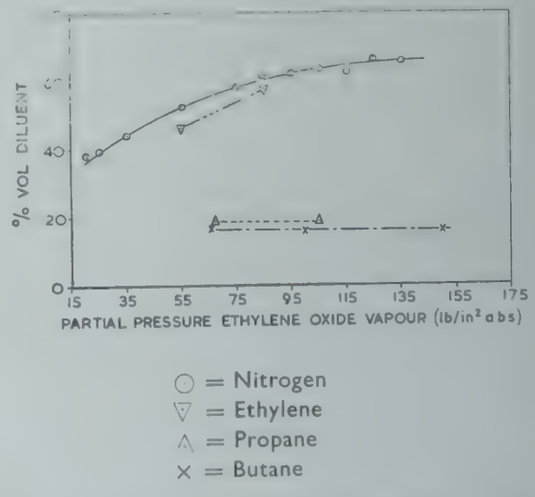


Fig. 7.—*The percentage of various diluents necessary to suppress the decomposition of ethylene oxide vapour at 125°C as a function of the partial pressure of ethylene oxide*

Over the temperature range 89–184·5°C the percentage of nitrogen needed to suppress the explosive decomposition of ethylene oxide under a partial pressure of 85 lb/in² abs was constant to within ±2%. Thus, within this range temperature appears to have very little effect on the limit of explosibility of ethylene oxide in nitrogen and, if it is assumed that this is true at a temperature of 60°C, then a comparison may be made between the results obtained by Hess and Tilton[12] and those from this investigation. Whereas the results given by Hess and Tilton indicate that 25% nitrogen will suppress

the explosive decomposition of ethylene oxide at a partial pressure of 75 lb/in² abs, those obtained in this investigation suggest that 58% nitrogen is necessary. If Hess and Tilton are correct in assuming that the partial pressure of the ethylene oxide vapour does not affect the proportion of nitrogen necessary to suppress the decomposition, then the discrepancy between the results indicates that much more inert diluent is needed to suppress the decomposition when it is initiated by a fused Nichrome wire, as in the present work, than when it is initiated by a heated platinum coil.

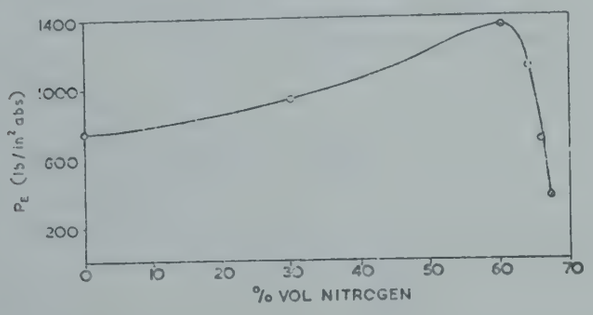


Fig. 8.—*The pressures developed on ignition of mixtures of nitrogen and ethylene oxide in which the partial pressure of ethylene oxide is 125 lb/in² abs*

In Fig. 8 the explosion pressures developed on igniting various mixtures of nitrogen and ethylene oxide at a constant partial pressure of ethylene oxide of 125 lb/in² abs are shown as a function of the percentage of nitrogen in the mixture. It may be seen that whereas the explosion pressure of pure ethylene oxide at a pressure of 125 lb/in² abs is 760 lb/in² abs that of a mixture containing 60% nitrogen is 1350 lb/in² abs. Thus for any application in which an inert diluent is required to suppress the decomposition of ethylene oxide it is important to ensure that *insufficient* diluent is *not* used. With ethylene oxide at a partial pressure of 125 lb/in² abs at least 67% of nitrogen is needed to suppress explosive decomposition at 125°C.

Table I gives the analysis of the gaseous products of decomposition from two experiments in which ethylene oxide at a partial pressure of 85 lb/in² abs was diluted with different amounts of nitrogen. These results show that the percentage of ethylene oxide in the decomposition products increases as the percentage of nitrogen in the mixture before ignition increases. At the limit, 61% nitrogen, all the ethylene oxide will remain undecomposed.

Effects of the internal size and shape of the vessel

The explosion vessel shown in Fig. 1 had an internal volume to surface area ratio, V/A, of 0·935 in³/in² and an internal volume of 148·9 in³. In order to investigate the effect of the size and shape of the container on the explosive decomposition of ethylene oxide two stainless steel, open-ended liners were provided, each of which fitted tightly into the explosion vessel. The first liner, which halved the internal volume of the vessel, was designed so that the ratio of the internal overall length to diameter, $L/D = 2{\cdot}25$, was the same as that of the original vessel. Although the internal shape of the explosion enclosure within this liner corresponded to that of the original vessel, the ratio V/A was 0·730 in³/in². The second liner was designed to decrease the ratio V/A to 0·238 in³/in²; this necessitated reducing the internal volume to 8·0 in³ and increasing the ratio L/D to 6·77. The effects of changing the size and shape of the explosion enclosure on the pressures developed during the decomposition of ethylene oxide and on the limit of explosibility of ethylene oxide in nitrogen are summarised in Table II. It would appear from the low values of P_F/P_I that decomposition may not have been complete in the case of the vessel having the smallest volume.

TABLE II.—*The Effect of the Size and Shape of the Container on the Explosive Decomposition of Ethylene Oxide*

	Vessel	Liner I	Liner II
Internal volume V (in³)	148·9	79·7	8·00
Ratio V/A (in³/in²)	0·935	0·730	0·238
Ratio L/D	2·25	2·25	6·76

Explosion of $(CH_2)_2O$ vapour at pressure P_I

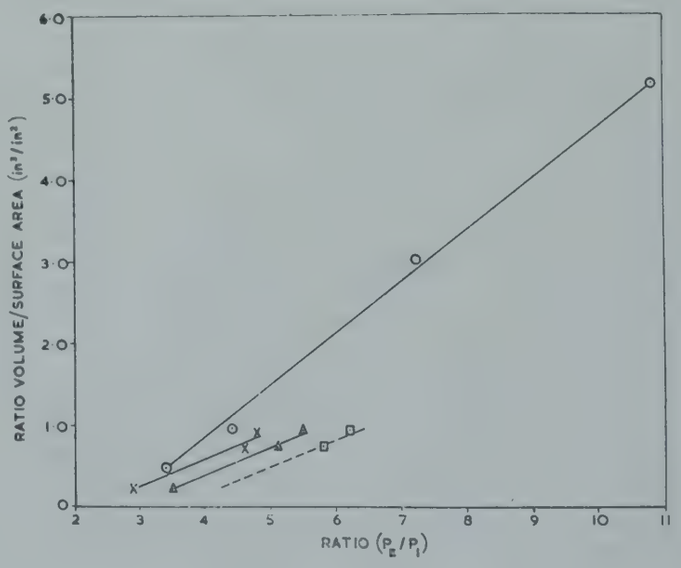
	Vessel			Liner I			Liner II		
P_I (lb/in² abs)	$\frac{P_E}{P_I}$	$\frac{P_F}{P_I}$	t* (s)	$\frac{P_E}{P_I}$	$\frac{P_F}{P_I}$	t* (s)	$\frac{P_E}{P_I}$	$\frac{P_F}{P_I}$	t* (s)
55	4·8	2·19	0·40	4·6	2·18	0·40	2·9	2·10	0·17
85	5·5	2·36	0·27	5·1	2·34	0·30	3·5	2·06	0·13
125	6·2	2·53	0·21	5·8	2·48	0·17	—	—	—

Explosive for $(CH_2)_2O$ vapour at partial pressure P_I in N_2

	Vessel	Liner I	Liner II
P_I (lb/in² abs)	Percentage nitrogen by volume		
55	52·3	56·2	—
85	61·4	61·4	65·4
125	66·5	70·7	—

* t = time to develop 90% of the maximum explosion pressure P_F.

In Fig. 9 the values of the ratio P_E/P_I obtained with the various liners are compared with those obtained by Hess and Tilton[12] using vessels which covered a wider range of ratios of volume to surface area.



○ = 20 lb/in² abs, 30-40°C[12]
× = 55 lb/in² abs, 125°C
△ = 65 lb/in² abs, 125°C
□ = 135 lb/in² abs, 125°C

Fig. 9.—*Effect of the ratio of volume to surface area on the explosion pressures developed during the decomposition of pure ethylene oxide*

Discussion

This investigation confirms that the observed limit for flame propagation in a mixture of ethylene oxide vapour and inert diluent depends on the energy of the igniting source. Although it was calculated, assuming that no heat was lost, that the energy needed to fuse the whole length of the standard 31 s.w.g. Nichrome wire was about 10 joules, only a small proportion of this would be transferred to the gas during the ignition process. Fig. 4 suggests that when the energy dissipated in the igniting source exceeds a certain critical value the explosive limit is independent of the size of the source. Thus the use of a source whose energy exceeds this critical value should ensure that the results are unaffected by minor variations in power input. It is believed that results similar to those in Fig. 4 would have been obtained using a low energy igniting source provided the energy was released very quickly as in a condenser spark.

The increase in the values of the ratios P_E/P_I and P_F/P_I as the initial pressure increases may be partly ascribed to the effect of pressure on the amount of ethylene oxide undergoing decomposition. The analyses in Table I showed that at an initial pressure of 45 lb/in² abs, 15·4% of the ethylene oxide remained undecomposed while at a pressure of 135 lb/in² abs the amount was less than 0·2%.

Although the non-explosive thermal decomposition of ethylene oxide vapour has been studied by a number of investigators[15–23] relatively little attention has been given to the mechanism of the explosive decomposition. Burden and Burgoyne[7] showed that the decomposition products at room temperature and atmospheric pressure given in Table III could be most simply explained by assuming the occurrence of two simultaneous reactions having the following overall effects :

$$C_2H_4O = CH_4+CO \quad .. \quad .. \quad (1)$$

$$2C_2H_4O = C_2H_4+2CO+2H_2 \quad .. \quad .. \quad (2)$$

It was concluded that during the explosive decomposition of ethylene oxide at room temperature and atmospheric pressure, 69% of the ethylene oxide decomposed in accordance with reaction (1) and 31% in accordance with reaction (2).

Most workers who have investigated the slow non-explosive decomposition of ethylene oxide have agreed that reaction (1) is prominently involved under their experimental conditions and Seddon and Travers[15] found evidence of reaction (2) as a significant parallel reaction. Heckert and Mack[16] and Thompson and Meissner[17] suggested that the following reaction occurs to a small extent, but they did not mention reaction (2).

$$2C_2H_4O = C_2H_6+H_2+2CO \quad .. \quad .. \quad (3)$$

The results obtained by Burden and Burgoyne could equally well be interpreted by replacing reaction (1) by a similar one involving a larger paraffin molecule such as reaction (3), but they found no evidence of such a reaction and it is certainly less probable than reaction (1).

The decomposition products obtained when ethylene oxide vapour, initially at a temperature of 70°C, is burnt in absence of air at atmospheric pressure in a flat flame burner[25] are given in Table III together with those formed when ethylene oxide is decomposed in a rocket motor[24] at a chamber pressure of 750±50 lb/in² abs. For comparison the analyses obtained during the course of the present investigation have been converted to an ethylene oxide free basis.

It may be seen from Table III that the chief effects of pressure are to increase the amount of methane and to decrease the amount of ethylene formed as a result of the decomposition. The heat liberated by reaction (1) is 32·11 K cal/mole whereas that by reaction (2) is only 7·98 K cal/mole. Thus the effect of pressure is to increase the overall heat of reaction. In addition to the gaseous products listed in Table III, solid carbon combined with a variable amount of hydrogen was deposited in the vessel at pressures in excess of atmospheric. It appears likely that this was formed by the exothermic pyrolysis of ethylene.

TABLE III.—*Effect of Pressure on the Gaseous Decomposition Products of Ethylene Oxide*

Constituent	Flat Flame[25] (%)	Flame propagation[7] (%)	Explosive decomposition (%)	(%)	Rocket motor[24] (%)
H_2	19·6	12·7	16·4	16·1	9·5
CO	44·3	46·6	48·7	47·1	48·5
O_2	—	—	—	0·2	—
CH_4	25·9	32·2	32·2	35·2	39·9
C_2H_6	—	—	1·3	1·0	2·1
CO_2	—	1·0	0·2	0·3	—
C_2H_4	10·2	7·5	1·2	—	—
P_I (lb/in² abs)	14·7	14·7	45	135	750±50

The laminar burning velocity of ethylene oxide vapour in absence of air at atmospheric pressure as measured in a flat flame burner[25] was only 4 cm/s ; this accounts for the slow rate of pressure increase shown in Fig. 6. Although dP/dt is increased as the initial pressure of ethylene oxide vapour is raised, the value at 45–55 lb/in² abs is still only 1300 lb/in² s. In view of this it is surprising that Hess and Tilton[12] were unable to use a bursting disc to relieve the pressure in their vessel.

The most important practical result of this investigation is that a much larger proportion of nitrogen has been found necessary to suppress the explosive decomposition of ethylene oxide than had been suggested by Hess and Tilton[12]. Presumably the reason for the widely differing results arises from a difference in the energy transferred to the gas by the two igniting sources. Furthermore the amount of nitrogen as shown in Fig. 7 increases with increasing partial pressure of ethylene oxide vapour in the mixture. This result is to be expected if the proposed mechanism of decomposition is accepted since the heat of decomposition of ethylene oxide will increase with pressure. In addition, pressure has the effect of increasing the burning velocity. Hence the heat losses will be reduced and more nitrogen will be required to absorb the heat liberated by explosive decomposition. Ethylene was not very effective in suppressing the decomposition because some of it decomposed to carbon and hydrogen and in so doing liberated heat. Propane and butane are more effective than nitrogen because of their greater heat capacities.

Since the burning velocity of the ethylene oxide decomposition flame is low, it is to be expected that the ratio of the volume to the internal surface area of the vessel will affect the explosion pressures developed owing to variation in heat losses. This is confirmed by the results given in Fig. 9 from which it may be seen that the ratio P_E/P_I decreases as the ratio V/A decreases. Having regard to the mechanism of the reaction, thermochemical calculations indicate that the ratio P_E/P_I will not exceed 10 at high initial pressures, even in vessels having a large volume to surface-area ratio.

Conclusions

It has been confirmed that ethylene oxide in the absence of air will undergo explosive decomposition at 125°C and

pressures up to 155 lb/in² abs when ignited with a source of suitable energy. The pressure rise within the vessel depends on the initial pressure of the ethylene oxide vapour and to a certain extent on the size and shape of the vessel. Under similar pressure and temperature conditions propylene oxide vapour was found to be stable but at higher pressures and temperatures it is thought that it too may be made to decompose explosively if ignited.

The use of an inert gas to maintain a non-explosive vapour-phase mixture is the only reliable method of preventing an explosion from ignition sources within a vessel. Although propane and butane are most effective in suppressing the explosive decomposition of ethylene oxide, in practice their use is restricted because of their solubility in liquid ethylene oxide. The proportion of nitrogen needed to suppress the explosibility of ethylene oxide at a partial pressure of 120 lb/in² abs and 125°C is 65%. It must be remembered that a small amount of oxygen or an increase in the partial pressure of ethylene oxide vapour will raise this figure ; hence in practice it might be necessary to increase the proportion of nitrogen to, say, 75% to cover these contingencies. This procedure necessitates designing the vessel to withstand a working pressure about four times the partial pressure of the ethylene oxide vapour.

An alternative procedure is to design the vessel to withstand the pressure generated by the products of combustion. Before this can be done with confidence it will be necessary to examine in more detail the effect of the size and shape of the vessel on the maximum decomposition pressure developed. Although it is considered unlikely that the pressure ratio P_E/P_I in a vessel having a large volume to surface area ratio will exceed 10, the possibility of a detonation cannot be discounted ; nevertheless, under conditions of size and pressure similar to those employed in this investigation, this seems unlikely.

Acknowledgments

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Appendix

Ethylene oxide was supplied by Petrochemicals Ltd. The analysis of the gas was as follows :—

Aldehyde content as acetaldehyde ..	% wt.	0·005
Water content	% wt.	<0·01
Hydrolysable chlorine as ethylene dichloride	% wt.	0·0037
Acetylene content	% wt.	<0·005
Ethylene oxide content	% wt.	>99·9

Nitrogen and ethylene were supplied by British Oxygen Gases Ltd.The nitrogen content on a dry basis was 99·9% vol, the oxygen content 0·05% vol, the remainder consisting of the rare gases together with traces of carbon dioxide and hydrogen. The ethylene content on a dry basis was greater than 98% vol, the chief impurities being nitrogen and carbon dioxide.

Butane and propane were supplied by Shell-Mex and B.P. Gases Ltd.

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EXPLOSION HAZARDS IN THE MANUFACTURE OF TEREPHTHALIC ACID

By D. H. DERBYSHIRE, B.Sc., D.Phil.*

SUMMARY

The manufacture of terephthalic acid by the oxidation of *p*-xylene with nitric acid involves an explosion hazard. This arises since the gases evolved during the oxidation are capable of supporting the combustion of *p*-xylene. The paper discusses this problem and indicates how the plant has been designed to operate safely.

The operation of the plant could have been safeguarded by the injection of inert gas but considerable quantities of inert gas would have been required and the process would have been costly to operate. Instead, each plant unit has been considered individually and separate safeguards were either incorporated into the design of each unit or into the method of operation. The safety of the oxidation autoclaves is ensured by keeping the partial pressure of the steam high enough to inhibit combustion. The explosion hazard in the condensing system is accepted and the unit is designed to minimise damage if an explosion occurred. Large storage tanks are necessary to enable the recovery of nitric acid to be carried out continuously and safety in these is ensured by keeping the *p*-xylene content below the lower limit of flammability.

An account is given of some of the experimental techniques and apparatus used to obtain basic data for the design and operation of the plant.

Introduction

Terephthalic acid is made in large quantities by Imperial Chemical Industries Limited as an intermediate in the manufacture of Terylene. *p*-Xylene is the raw material and this is oxidised in one stage to terephthalic acid using nitric acid as the oxidising agent at elevated temperatures and pressures. The process involves an explosion hazard and it is proposed to discuss this problem and to describe the apparatus and techniques used to obtain the data required to enable the plant to operate both safely and economically. For obvious reasons it is not possible to describe the plant in detail but the type of plant involved and the method of operation is outlined briefly and in general terms, below.

Outline of the process

A diagrammatic flowsheet of a terephthalic acid plant is given in Fig. 1.

The oxidation is a batchwise one and is carried out in the autoclave, A. *p*-Xylene and nitric acid are introduced into the vessel, steam heating applied and the temperature and pressure brought to the operating conditions. The control parameter is the pressure which is defined by the control valve, C.

The evolved gases, consisting of nitrous oxide, nitric oxide, nitrogen, and carbon dioxide, are passed through the condensing system and condensed material returned to the autoclave. The gases then pass through the pressure control valve and are stored in the buffer tanks, D.

Large buffer tanks receive gas under pressure from a number of autoclaves. The vessels have large capacity and smooth the gas flow from the batchwise oxidations so enabling the recovery of nitric acid to proceed in a continuous manner. They are thus very important ; a single autoclave being out of action is not critical but damage to the buffer tanks would close the whole plant.

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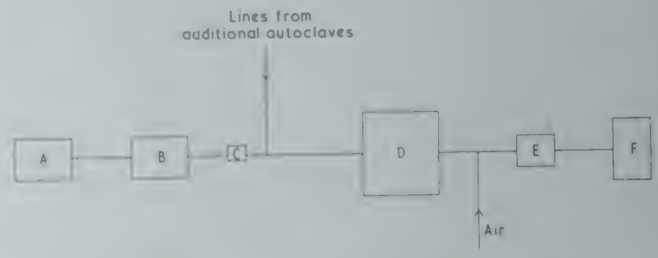


A = Autoclave
B = Condensing system
C = Control valve
D = Buffer tanks
E = Oxidiser cooler
F = Absorption tower

Fig. 1.—*Diagrammatic flowsheet of terephthalic acid plant*

The gas containing nitric oxide is passed from the buffer tanks to the oxidiser-cooler, E, where, after admixture with air, the nitric oxide is oxidised to nitrogen dioxide. The absorption of nitrogen dioxide to give nitric acid is carried out in the absorption tower, F.

Nature of the explosion hazard

The mixture of nitrogen oxides generated during the oxidation is capable of supporting the combustion of *p*-xylene. There is, therefore, the danger of a vapour-phase explosion in the autoclaves, condensing system, buffer tanks and oxidiser-cooler. In the oxidiser-cooler, however, there is an additional danger. Under certain conditions organic material may separate out as a liquid phase and dissolve nitrogen dioxide to form a potentially explosive liquid. Liquid mixtures of this type constitute the well-known Sprengel-type explosive.

In safeguarding the plant no attempt has been made to track down and eliminate all possible sources of ignition. The approach has been either to operate the plant so that the vapour spaces of the various units are filled with non-flammable gas or, when this is impossible, to design the plant to minimise explosion damage.

It would have been possible to safeguard the plant, with the exception of the oxidiser-cooler, by the injection of inert gas. This would have required the nitrogen content of the evolved gases to be raised to about 60% and would have made the process extremely costly to operate. Instead each plant unit has been considered independently.

Safety in the autoclave is achieved by operating at such a temperature that the amount of steam in the vapour space is sufficient to prevent an explosion. Clearly, it is impossible to operate the condenser under such conditions and the explosion risk in this vessel has been accepted. The vessel has been designed to minimise damage if an explosion occurs and venting devices have been fitted to prevent explosion pressures from being transmitted to the autoclave. The *p*-xylene in the gas passed to the buffer tank is measured and if this exceeds the lower limit of flammability inert gas is injected and the plant is closed down. The oxidiser-cooler is carefully designed to be self-draining to the absorption tower. As an additional safety measure the large plant units, *i.e.* autoclaves, condensers, and buffer tanks, are operated behind blast walls.

The safety precautions taken in the operation of each unit are described in the following sections.

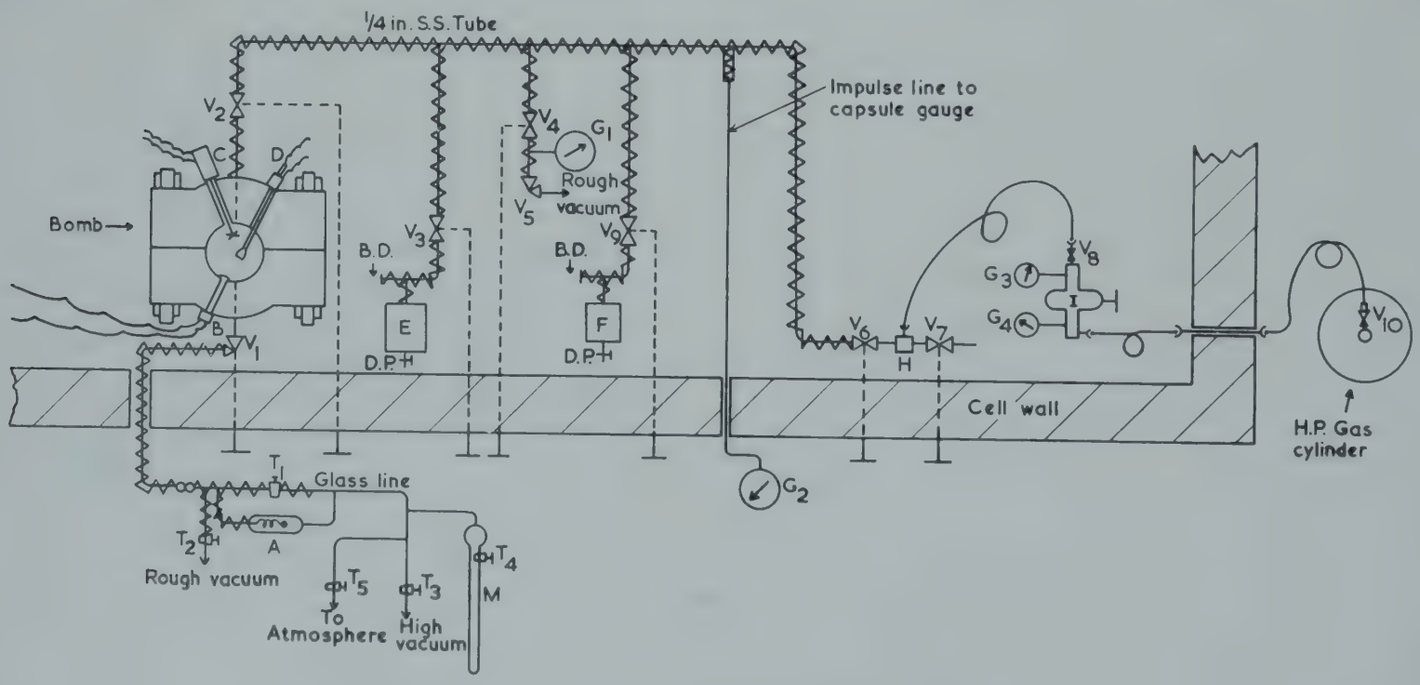
Safety in Individual Plant Items

Autoclave

The problem in connection with the autoclave is to define a safe minimum temperature so that the amount of steam in the vapour is great enough to keep the gas non-flammable. If the temperature falls below this point the batch is stopped and the pressure reduced, so displacing the gas in the autoclave by steam. It is of some importance to define this minimum safe temperature fairly accurately. If it is too low there is the danger of producing an explosive gas mixture. If it is higher than necessary batches are stopped unnecessarily and production is curtailed and cost increased.

Experimentally, it is somewhat complicated to determine this minimum operating temperature since the process is operated batchwise and conditions in the autoclave change as the oxidation proceeds. The main gaseous products are nitric oxide and nitrous oxide and the proportion of these in the evolved gases alters throughout the oxidation cycle. To limit the work involved and to simplify plant operation, it was necessary to determine which was the most dangerous mixture and then to carry out experimental work with gas of this composition. This was relatively easy since it was found that the limits of flammability of *p*-xylene in nitrous oxide were wider than in nitric oxide. Attention was therefore centred on the gas mixture containing the maximum ratio of nitrous oxide to nitric oxide. It is an added complication that the partial pressure of *p*-xylene in the autoclave changes as the reaction proceeds. Initially, the mixture in the autoclave consists of two liquid phases : (1) dilute nitric acid and (2) *p*-xylene. The gas space above the liquid contains gas saturated with water and *p*-xylene at the temperature of the autoclave. As the reaction proceeds the liquid *p*-xylene disappears and hence the partial pressure of *p*-xylene in the gas phase falls from its equilibrium value at this temperature to a very low value depending on the degree of completion of the reaction. Since the partial pressure of *p*-xylene is not strictly defined it is quite impossible to operate above the upper limit of flammability ; safety must, therefore, be based on steam pressure alone.

The safe temperature was determined by measuring the limits of flammability of *p*-xylene in the most dangerous gas and investigating the effect of steam on these limits. The apparatus is shown diagrammatically in Fig. 2. It consists



∧∧∧∧∧∧∧ = Heated and lagged lines

A = Gass spiral gauge	E, F = Boilers	M = Manometer
B = Transducer	G = Gauges	T = Glass taps
C = Magnetic stirrer	H = Manifold	V = Valves
D = Ignition source	I = Reducing valve	B.D.= Bursting disc
		D.P.= Drain plug

Fig. 2.—*High pressure explosion apparatus*

of a bomb with a spherical cavity in which gas mixtures are made and tested for flammability. Two bombs are available, one having a capacity of three litres and the other a capacity of six litres. Connected to the bomb are two heated boilers, E and F, which can be used as reservoirs of steam or flammable vapour. The connections in the apparatus are by lens-ring joints and the system will withstand pressures of the order of 3–4000 lb/in² and in addition can be evacuated down to pressures of 10^{-3} mm Hg. The latter condition is necessary since gas mixtures are made up by the method of partial pressures.

Gas mixtures are made up in the bomb by admitting the required vapours at defined pressures and then adding oxidising gas to the required total pressure. Vapour pressures up to about 1·5 atmospheres are measured with a glass spiral gauge, A, used as a null instrument, but above this pressure the capsule Budenburg gauge, G_1, with the capillary impulse line is used. The oxidising gas is then added using the remote controlled operating valves and measuring the pressure by the capsule Budenburg gauge, G_2, outside the cell. The gases in the bomb are thoroughly mixed by the totally-enclosed magnetic stirrer, C, and then tested for flammability by fusing a wire positioned in the centre of the spherical cavity. The rise in pressure is used as the criterion of flammability. This is measured by the transducer, B, the signals from which are amplified and then displayed on a cathode-ray oscilloscope ; the transducers used are either diaphragm or strain-gauge type instruments. The ignition source was chosen after experiments with hot wires and high tension sparks had shown that the measured limits of flammability were independent of the type of ignition source. The flammability determinations were carried out at the autoclave operating pressure and at a fixed temperature near to the expected minimum safe temperature. The precise temperature is unimportant provided it is sufficiently high to keep the steam and *p*-xylene in the vapour phase. The results are shown diagrammatically in Fig. 3. The apices of the triangle represent steam, *p*-xylene vapour, and reaction gas under the given conditions, and the area within the triangle therefore

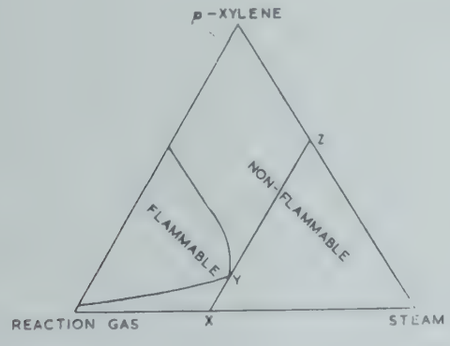


Fig. 3.—*Diagrammatic representation of limits of flammability for autoclave gases*

represents mixtures of these compounds. The safe operating conditions are represented by the area to the right of the line X–Y–Z. This line represents the minimum steam partial pressure required to suppress the combustion of *p*-xylene in reaction gas. The temperature at which the water vapour pressure becomes equal to this pressure is the minimum safe temperature of autoclave operation.

Condenser

As the gas from the autoclave passes through the condenser, steam and *p*-xylene are stripped out and the gas mixture passes through the flammable region. The approach has been to accept this and to build the plant to minimise damage if an explosion occurs rather than to render the gas non-flammable by the injection of inert gas. It is also believed that any potential source of ignition would be in the hot autoclave and not in the relatively cool condenser. Since the autoclave is operated under non-flammable conditions this adds a further margin of safety.

The condensers have been made to withstand the maximum computed explosion pressures. These pressures, calculated according to simple thermochemical principles neglecting the dissociation of combustion products and cooling, are in the region of 3000 lb/in². To prevent dangerous pressures from being transmitted to the autoclaves, bursting discs have been fitted to the condenser and to the autoclave. Since right-angle bends occur at each end of the condenser, bursting discs have been placed at each corner in line with the condenser tubing. It is considered that bursting discs in these positions would be very efficient but no experimental work has been carried out to prove this. Assuming an instantaneous rise in pressure to 3000 lb/in² in the condenser it has been calculated that these discs would prevent the pressure in the autoclave rising above the test pressure.

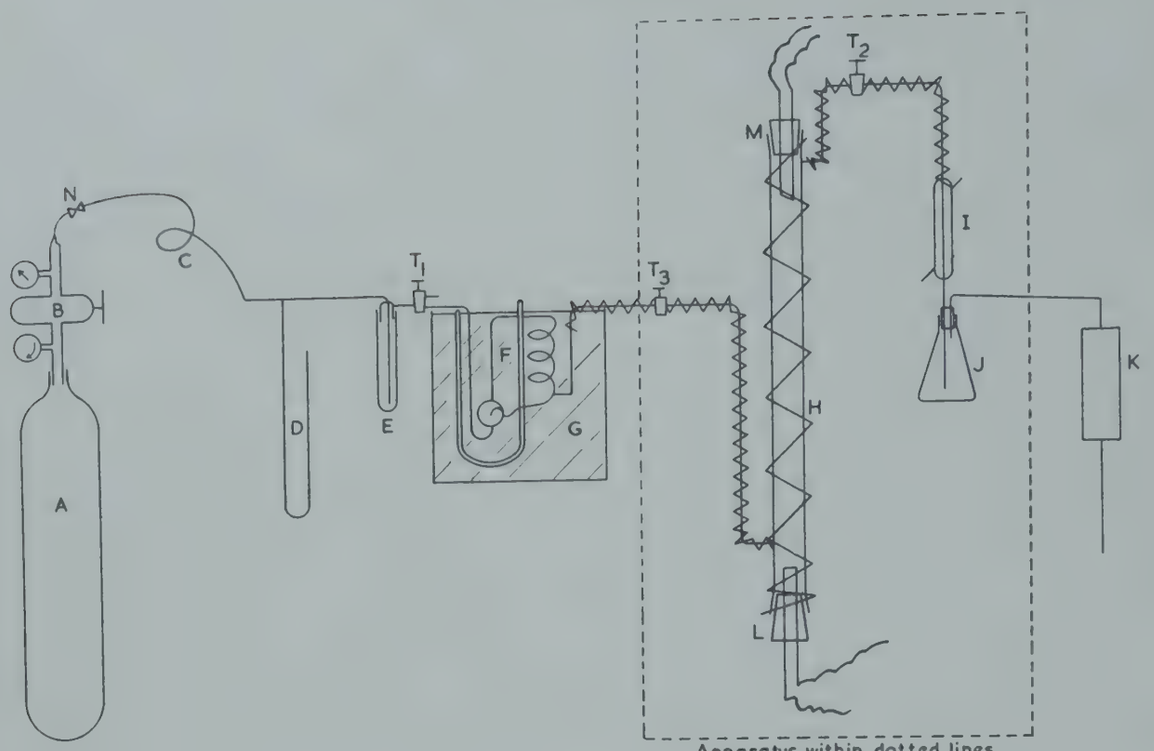
In calculating the explosion pressures it has been assumed that hydrodynamic effects in the combustion process were absent. No attempts have been made to determine the ability of these gas mixtures to propagate a detonation wave. If a detonation wave were propagated the pressures in the Chapman–Jouguet zone would be about 6000 lb/in². Approximate calculations have been made taking into account the very short times during which these pressures would be exerted and these show that the condenser would probably withstand these pressures. The very high pressures frequently observed prior to the initiation of a stable detonation wave would probably damage this plant unit but it would be quite uneconomic to attempt to guard against this.

To prevent injury to personnel each autoclave and condensing system is isolated in a separate blast cubicle.

Buffer tanks

The gas from the autoclaves is stored in the buffer tanks at elevated pressures and ambient temperatures. The gas contains nitric oxide and nitrous oxide in the ratio of $NO : N_2O = 2 : 1$ with about 20% by volume of inert gas (carbon dioxide and nitrogen). Since the tanks are operated continuously, the gas composition remains sensibly constant.

The limits of flammability of *p*-xylene in this mixture of nitrogen oxides and the effect of nitrogen on these limits have been investigated at atmospheric pressure and higher pressures to cover the operating conditions of the tanks. The experiments under pressure were carried out using the spherical bomb described above ; the limits at atmospheric pressure were determined using the apparatus shown diagrammatically in Fig. 4. A flow technique is used to obtain mixtures of fuel and oxidising gas of known composition. Synthetic gas mixtures contained in the cylinder A are passed through a saturator, F, G, containing the fuel and saturated with the vapour of the fuel at a definite temperature. The saturator consists essentially of a high temperature bath, F, situated inside a low temperature bath, G ; the low temperature bath is maintained accurately at a given temperature whilst the high temperature bath is kept about 15°C hotter.



A = High pressure gas cylinder
B = Reducing valve
C = Rubber tubing
D = Di-butyl phthalate manometer and blow-off
E = Cold trap
F = High temperature bath of saturator
G = Low temperature bath of saturator
H = Flame tube (heated)
I = Condenser
J = Catch pot
K = Flowmeter
L = Cap holding ignition source
M = Cap holding flame detector
N = Needle valve
T_1 = Three-way tap
T_2 & T_3 = Two-way taps

Fig. 4.—*Schematic diagram of atmospheric pressure explosion apparatus*

The gas is bubbled through a vessel containing fuel in the high temperature bath and then passed through a cooling coil in the low temperature bath. In principle, therefore, the gas is " over-saturated " with fuel vapour in the bath, F, and then brought to equilibrium saturation with vapour at the temperature of the bath, G.

In this way a gas stream can be accurately saturated with vapour at flow rates of about a litre per minute. The mixture of gas and vapour is then passed to the long tubular vessel, H, where it is tested for flammability. If saturation is carried out a temperature higher than ambient then the lines from the saturator and the tube H are heated to prevent condensation. The tube H is a glass tube 4 ft long and 2 in. internal diameter. It is surrounded by a slightly wider tube serving as a former for the electric heating wires and by an additional thick-walled " Visible Flow " tube acting as a thermal shield and as a protection against flying glass in the event of the rupture of the flame tube. A flammability determination is made by closing the taps T_3 and T_2, withdrawing the cap L and then attempting ignition using the source L which may be a high-tension spark or a hot wire. The criterion of flammability is the distance a flame travels up the flame tube after attempted ignition, the limit composition being taken as that mixture in which a flame is propagated just short of the full length of the tube. The ignition source was obviously more than adequate since near the limits flames could be initiated which only travelled part of the way up the tube. Some flames are difficult to detect visually but additional help is given by the flame detector, M, which consists of a thermocouple or thermistor.

To determine the amount of nitrogen required to inhibit the combustion of *p*-xylene in these gases the experiments were carried out at 100°C. in order to provide sufficient *p*-xylene in the vapour phase. The results at atmospheric pressure are shown in Fig. 5 ; increasing pressure widens the limits.

Under normal operating conditions the content of *p*-xylene of the gas from the autoclaves is quite well removed from the lower limit of flammability. Certain abnormal operating conditions, *e.g.* an overloaded condensing system, could, however, increase the content of *p*-xylene above the lower flammability limit. If the content of *p*-xylene reaches about half the lower limit value inert gas is injected and the plant closed down for investigation.

The method of measuring the content of *p*-xylene is novel and perhaps of interest. Since the gas contains small amounts of nitrogen dioxide infra-red and ultra-violet techniques cannot be used. A bleed of gas is taken from the manifold leading to the buffer tanks and the pressure reduced to atmospheric pressure in order to evaporate any mist that might be

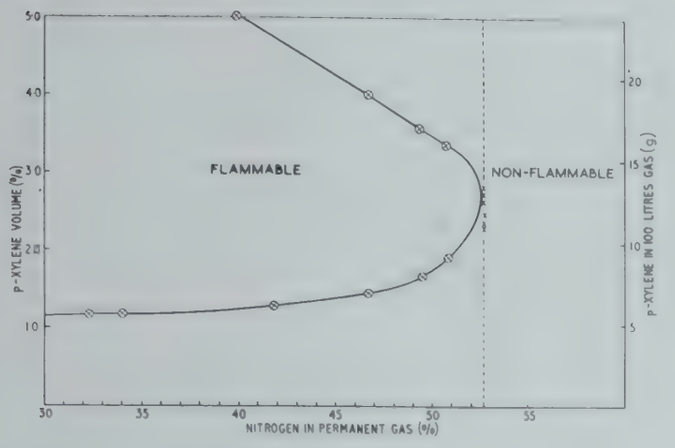


Fig. 5.—*Effect of nitrogen on limits of flammability of p-xylene in a mixture of nitric oxide and nitrous oxide* ($NO : N_2O = 2 : 1$) *at atmospheric pressure.*

present. The gas is then passed through a bed of catalyst and the *p*-xylene oxidised to carbon dioxide and water. The rise in temperature of the bed is a measure of the *p*-xylene concentration. The instrument is, of course, fitted with flame traps to prevent " flash-back ".

Eventually, it is hoped that the *p*-xylene monitor will automatically inject gas when the *p*-xylene reaches a dangerous level. Inert gas would then be injected to make the gas entering the buffer tank non-inflammable and also to ensure that the gas mixture remained non-inflammable after admixture with the buffer tank contents.

Oxidiser-cooler

The gas from the buffer tanks is mixed with about four times its volume of air and passed to a long water-cooled tube called the oxidiser-cooler where exothermic reaction occurs to give nitrogen dioxide.

The amount of *p*-xylene vapour present is below the lower limit of flammability and hence under normal conditions there is no danger of a gas-phase explosion. However, it has been found that chemical reaction occurs between the *p*-xylene vapour contained in the gas from the buffer tanks and the nitrogen oxides to give the less volatile nitrated compounds. On cooling the gas these nitro-compounds separate out as a liquid phase and dissolve nitrogen dioxide, forming a liquid mixture which has been shown to be capable of detonation. To minimise the hazard the coiled pipes of the oxidiser-cooler and the gas line leading to the absorption tower have been carefully positioned so that the complete system is self-draining to the absorption tower. Liquid cannot accumulate in the system in any significant quantity. It has also been shown that the thin film of liquid in the pipe is not sufficient to rupture it in the event of detonation occurring. The nitro-xylenes are also sufficiently soluble in the strong acid at the base of the tower to be removed in solution in the recovered acid. The potential hazard has, therefore, been reduced to a minimum.

Conclusions

The work done on explosion hazards has enabled changes to be made in the terephthalic acid plant, which cannot be detailed here, but which have increased safety without affecting economic production. It is hoped that this review will be of value in assisting others to attack similar problems.

Acknowledgment

All the experimental work described in this paper was carried out in conjunction with Mr. A. D. Craven.

The manuscript of this paper was received on 14 *March*, 1960.

DISCUSSION OF PAPERS PRESENTED AT THE SECOND SESSION

Dr. R. N. LACEY asked if Dr. Burgoyne could indicate whether in a cylindrical vessel with the ratio L/D appreciably greater than 1, it would be preferable to place the explosion relief vent at one end of the vessel at right angles to the longitudinal axis, or to place it nearer the middle of the vessel, parallel to that axis.

Dr. BURGOYNE replied that it was best to have the vent as near the source of ignition as possible. If a particular source of ignition was suspected, he thought that that would be the over-riding consideration. Otherwise, he felt that the question was more relevant to the paper presented during the third session on "Explosion Reliefs for Duct Systems" which related to venting of longer chambers and venting in pipelines.

Mr. P. VENEMA asked Dr. Burgoyne if he would expect to get different results from exploding pentane vapour or mixture in a sphere, and what the effect of the location of the ignition point in a sphere would be.

Dr. BURGOYNE replied that if a mixture in a sphere were ignited at the centre, the flame-front, in principle, reached all points on the vessel wall at the same moment. In those circumstances the pressure rise stopped abruptly and the explosion was complete in the shortest time possible for the volume of mixture concerned. In practice, convective effects upset the symmetry of the system to some extent. On the other hand, if the vessel were not spherical, the explosion flame reached certain parts of the vessel wall before others, with the result that the duration of the combustion was extended and the pressure rise ceased more gradually.

Dr. J. F. PRESTON said that he had understood Dr. Burgoyne to say that the pressure throughout the vessel was fairly uniform during the pressure rise. He wondered how Dr. Burgoyne and his colleagues had identified that experimentally.

Dr. BURGOYNE replied that the point had not been investigated in their experiments, but the pressure was communicated throughout the vessel at pressure wave velocities which were large compared with the rate of progress of the flame front. It was generally agreed that, in a compact vessel where no great distances were involved, the pressure could be taken as being uniform. He and his colleagues had nothing new to say on that subject.

Mr. R. H. B. FOSTER said that Dr. Burgoyne and his colleague had brought out a very important point: that a relief valve was better than a bursting disc as a safety device. He asked whether, in many cases, it would be necessary to employ a bursting disc because the relief valve would be of too great a size for practical purposes.

Dr. BURGOYNE replied that there might be that reason, and other reasons as well, for preferring a bursting disc. In the paper, they were merely pointing out that, other things being equal, one did get rather better performance in some circumstances with the smoothly-operating device. He thought that there was one practical advantage possessed by a hinged flap or spring-loaded valve; it could be made mechanically quite strong to external influences while still being capable of relieving internal explosion readily.

Dr. W. E. F. NAISMITH asked Dr. Bett what explanation he had for the increase in the explosion pressure of ethylene oxide when nitrogen was added. Normally, when nitrogen was added, the explosion pressure was reduced. From Fig. 8 in the paper by Burgoyne, Bett, and Muir, however, the explosion pressure appeared to rise to a maximum at about 60% nitrogen, and then decrease until at about 67% nitrogen the mixture was non-explosible.

Dr. BETT replied that Fig. 8 showed the maximum pressures developed on igniting various mixtures of nitrogen and ethylene oxide in which the partial pressure of the latter was maintained constant at 125 lb/in^2. Thus the total pressure of the gas mixture before ignition increased as more nitrogen was added to the ethylene oxide and that accounted for the increase in the explosion pressure as the nitrogen content of the mixtures was raised from 0 to 60%. On the other hand, the ratio of the maximum explosion pressure to the total initial pressure decreased from 6·1 to 4·3 over the same range of composition. The reason for that was that an increase in the proportion of nitrogen decreased the amount of ethylene oxide which decomposed. When the nitrogen content exceeded 60% the effect was pronounced and resulted in a marked decrease in the ratio of the maximum explosion pressure to the initial pressure. At the limit, 67% nitrogen, all the ethylene oxide remained undecomposed and the ratio was unity. That served to show that, for any application in which an inert diluent was required to suppress the decomposition of ethylene oxide, it was important to ensure that sufficient diluent was used.

Mr. J. R. BLANCO said that his impression on reading the paper of Hess and Tilton was that they were referring throughout to total pressure in their storage vessels. Referring to Table I in the paper by Burgoyne, Bett, and Muir, if that were the case, it would mean that their initial partial pressure was, in fact, about 18 lb/in^2 gauge. By reference to Fig. 7 of the paper that would correspond to a nitrogen percentage of about 42% volume. He asked for Dr. Bett's comments on that.

He also asked if Dr. Bett ascribed the different effects of the different metallic igniting elements to a catalytic influence.

Dr. BETT replied that Hess and Tilton gave the percentages of various diluents needed to suppress the explosive decom-

position of ethylene oxide at an initial pressure of 30 lb./in²g. Unfortunately it was not clear whether the pressure was the partial pressure of the ethylene oxide vapour or the total pressure of the gas mixture ; furthermore, the temperature at which the experiments were carried out was not stated explicitly. In preparing Table II (page 34) he and his co-authors assumed that the pressure referred to the initial pressure of ethylene oxide vapour before the inert diluent was added, and that it corresponded to the vapour pressure of ethylene oxide at about 43° C. If the alternative interpretation were correct, then the pressure of ethylene oxide must have been adjusted for each diluent investigated ; in the case of hydrogen and nitrogen it would have been about 33.5 lb/in² while in the case of butane 43.5 lb/in². As Mr. Blanco pointed out, that assumption reduced the difference between the percentage nitrogen needed to suppress the decomposition of ethylene oxide at a partial pressure of 33.5 lb/in² found by the authors and that found by Hess and Tilton, to 42%–25% *i.e.* 17%. In the other hand, Hess and Tilton assumed that the partial pressure of ethylene oxide in the range 15 lb/in² to 75 lb/in² had no effect on the percentage of nitrogen needed to suppress the explosive decomposition; thus, the discrepancy between the two sets of results depended on the pressure at which the comparison was made.

Dr. BURGOYNE said that he thought that the catalytic properties of the igniting elements were not important. Burgoyne, Bett, and Muir had, by their method, communicated more energy to the gas by the source of ignition than had Hess and Tilton. It would be noticed that they had investigated, to some extent, the effectiveness of the source of ignition, and the energy needed to get what seemed to them to be rational results. They had felt that Hess and Tilton did not, in fact, use a sufficiently energetic source, and also, did not use the most favourable type of source. It had been shown, for example, with the explosive decomposition of acetylene that fusing wires were more effective and reliable sources of ignition than just heated wires. The present authors thought their own source of ignition was more reliable and effective than Hess and Tilton's and therefore gave realistic results.

Mr. K. N. PALMER asked the authors whether any consideration had been given to using an explosion inhibitor rather than an inert blanketing material such as nitrogen ; in that case, one might be able to use an amount smaller than the rather large quantities of nitrogen required.

Dr. BURGOYNE said that they had not given any particular consideration to the point. He was not, at the moment, aware of any powerful inhibitor of the decomposition reaction. A mild retardant would be unlikely to have any significant effect upon the flame reaction involved in the explosion.

Mr. P. VENEMA said that perhaps carbon dioxide might act as an inhibitor.

Dr. BURGOYNE said that Hess and Tilton had tried carbon dioxide and had found it was a little, though not much more, effective than nitrogen. That would be expected on the grounds of its greater heat capacity and it did not seem as if any chemical inhibitory effect was involved.

Mr. C. A. CROSS asked about the apparatus used for the ethylene oxide decomposition. He had noticed that the pressures seemed to rise toward the design limit of the apparatus. He had looked through the paper by Burgoyne, Bett, and Muir, and could not see any provision in the way of relief. How would the apparatus have failed if, by some change, pressure had gone above the design limit ; was apparatus standing the middle of a laboratory, or was it properly protected ?

Dr. BETT said that no relief against over-pressure was provided for the explosion vessel. Since the vessel was designed so that the inner layers of the steel vessel would be on the point of yielding under a static pressure of 3000 lb/in², it should have been capable of withstanding a dynamic load of 1500 lb/in² without yielding, even if the loading had been instantaneous. In practice it was found that the minimum time taken to develop the explosion pressure was over 1000 times greater than the calculated natural period of vibration of the cylindrical part of the vessel. Under those conditions the loading was virtually static and the bursting pressure of the vessel was predicted to be about 6000 lb/in². Thus the factor of safety, based on the bursting pressure, was estimated to be about 4 at the maximum operating pressure. Since the steel used for the pressure vessel was very ductile and since care was taken in the design to eliminate, as far as possible, all stress raisers, brittle failure was considered unlikely and the vessel was located in a corner of the laboratory without any protection other than that afforded by its electrically heated oven.

If, by some chance, the pressure had continued to rise above 1500 lb/in², the authors consider that failure would have occurred at the semi-confined nickel gasket which formed the joint between the head and the body of the vessel. If, in the absence of any leakage at the mechanical joints, the pressure had continued to rise, the body of the vessel would have deformed considerably and then burst. The mode of failure in this case would probably have taken the form of a longitudinal crack.

Dr. D. J. LEWIS asked if Dr. Burgoyne's conclusion about a relief valve behaving more effectively than a bursting disc would apply to a fast explosion such as one would get from an hydrogen/air mixture.

Dr. WILSON replied that, in general, the allowable opening-time of a relief-valve increased with the dimensions of the vessel and decreased with increase in the burning velocity of the explosive mixture. In their work it was easy to make the opening-time much shorter than the duration of the explosion, but with fast-burning mixtures, particularly in small vessels, it might be difficult to achieve. A bursting disc might then be preferred, especially if the shock of its bursting did not cause a significant increase in the rate of combustion.

Dr. G. R. FULTON referred to a statement that propylene oxide was stable under conditions which caused ethylene oxide to decompose explosively but that under higher temperatures and pressures it may be made to decompose. What evidence was there of that ? Had the authors done any work on it ? What were the limits for propylene oxide ?

Dr. BETT stated that the authors had attempted to decompose propylene oxide vapour at a temperature of 125° C and pressures up to 165 lb/in² but they had not observed any decomposition using a fused nichrome wire as the source of ignition.

Dr. BURGOYNE said that propylene oxide was capable of exothermic decomposition, and one believed therefore, that at a sufficiently high pressure and temperature it would be capable of sustaining a decomposition flame ; but they could not make any prediction as to the temperatures and pressures concerned. The authors could only report the negative results of their tests up to 165 lb/in^2 at 125° C.

Mr. D. R. M. FRYER asked if Dr. Derbyshire could say something about the basis used for the design of the blast walls surrounding the equipment.

He was thinking in terms of relating the explosion in the vessel to the effective wall strength and other factors such as vessel design and location.

Dr. DERBYSHIRE said that the design of the blast walls surrounding the equipment was the responsibility of the Division Engineering Department. Research Department either computed or measured the maximum explosion pressures that would be reached in the various plant units in the event of an explosion. Using that basic data Engineering Department then designed the blast walls in conjunction with the explosive experts at Nobel Division.

Mr. V. KENWORTHY said that Dr. Derbyshire relied on the fact that the plant protection against a back blow from the condenser to the autoclaves was insured because the partial water vapour pressure was high when the plant was running. Did that apply when they were starting up and closing down the plant ?

Dr. DERBYSHIRE said that although it was certain that the gaseous contents of the autoclave were non-flammable once normal operating conditions had been reached, it was quite possible that during the start-up of a batch, when the temperature and pressure were uncontrolled, the composition of the gas might pass through the flammable region. At the beginning of a batch the autoclave was pressurised with nitrogen but this would probably be insufficient to keep the gas non-flammable. During the main part of the oxidation and during the pressure let-down at the end of a batch, when the temperature and pressure were controlled, the gas in the autoclave was non-flammable.

Dr. L. COHEN asked if it was possible to say what was the nature of the ignition source one could expect.

Dr. DERBYSHIRE replied that possible ignition sources were numerous. There were many intermediate oxidation products which, in the presence of nitric acid might undergo exothermic decomposition and serve to ignite an explosion. Another possible source was a discharge of static electricity. However, very little work had been done in attempting to define the nature of the ignition source.

Mr. K. M. HILL said that Dr. Derbyshire seemed to have based the safety of the plant on the isolation of the individual items : for example, he had paid particular attention to that approach on the condenser, where he had the bursting discs at either end at the right angle bend. What would Dr. Derbyshire expect to happen in the way of second order effects ? The bursting disc had gone, the very high pressure had been relieved, but quite considerable pressures were travelling around the system which could cause physical mixing of the materials, changes to conditions outside the operating limits in the original autoclave, and similar effects going right through the baffle tank.

Dr. DERBYSHIRE said that if an explosion occurred in the condenser, then the relative volumes of the condenser and buffer tank were such that the gas coming from the condenser would not significantly alter the composition of the gas in the buffer tank. Did Mr. Hill mean that oxidising gas from the condenser might be passed into the autoclave and so produce an inflammable gas mixture ?

Mr. HILL said that when there was an explosion, there was nothing that he could see to stop the distribution of the contents of the autoclaves throughout the whole system. Pressure and vacuum waves were typical of such an event and it seemed to him that there was not, then, positive isolation.

Dr. DERBYSHIRE said that the pressure control valve effectively isolated the condenser from the buffer tank ; the contents of the autoclave could not be passed to the buffer tank. It was true that there was no positive isolation between condenser and autoclave but in the event of an explosion in the condenser it was improbable that the high pressure gas would get into the autoclave fast enough to pressurise it to any significant extent.

Mr. E. WALLER asked if it was not possible to get a build-up of nitro-compounds in the nitric acid and still form dangerous gases. Because the nitro-compounds were absorbed in the nitric acid and the nitric acid was re-used.

Dr. DERBYSHIRE replied that the nitric acid at the end of a batch was thrown away ; the recovered nitric acid came from the nitrogenous gases evolved during the oxidation. There was, therefore, a purging out of the system and the concentration of nitro-compounds did not build up.

Mr. C. A. CROSS asked what sort of arrangements were made to deal with the rather unpleasant materials that would be discharged if one of the safety devices ruptured, particularly on the condenser, in the event of an explosion in the condenser.

Secondly, on the use of a device to monitor the *p*-xylene content of the gases leaving the condenser, he always felt that continuous sampling devices involved a long time lag and were often somewhat unreliable. Had the possibility been considered of using a gas exit temperature from the condenser as a warning, because it seemed to him that, if action was taken when that temperature rose above the critical level, probably all eventualities would be covered.

Dr. DERBYSHIRE said that the buffer tanks and autoclave and condensing systems were behind very high blast walls. The explosion vents were arranged so that in the event of bursting, the liquid would not be projected over the blast walls. After such an event the enclosure within the blast walls would be washed down with water.

The temperature of the gas leaving the condensing system was in fact measured, but this did not define the *p*-xylene content of the gas since the *p*-xylene could be carried over as a fine mist or spray. The lag involved in continuous sampling had been reduced to negligible proportions.

Dr. C. A. CURTIS said Dr. Derbyshire had mentioned that some nitrogen oxide was absorbed by the nitro-compounds

and the explosive mixture then was soluble in the nitric acid and went to the bottom of the absorber. Was the nitric acid used later on, again in the oxidation process ?

Dr. DERBYSHIRE said that the recovered acid from the absorber was mixed with fresh acid and used again. The amount of nitro-xylenes present in the recovered acid was extremely small.

Mr. E. PENNY asked if Dr. Derbyshire had any trouble with the maintenance of the bursting discs at the end of the condenser.

Dr. DERBYSHIRE said that was a problem but there was a standard bursting disc change after a definite number of batches. It was rare that a disc failed prematurely due to corrosion.

Mr. D. ORMSTON asked if the plant as described in the paper was as it had originally been designed or had it been found necessary in the light of experience to carry out modifications for safety reasons. Had there been, in fact, any explosions on the plant?

Dr. DERBYSHIRE said that quite a few alterations had been made for safety reasons in the light of experience.

His colleague, Dr. GOODINGS, said that no major incidents had occurred on the plant.

Mr. F. REVILL said that, with regard to the chemicals used, it seemed that the plant might be weakened by corrosion and asked if special precautions had been taken on that account.

Dr. DERBYSHIRE said that he could not give an authoritative reply to the question. The plant had been constructed of a certain type of stainless steel with a corrosion allowance and no trouble had been experienced with corrosion.

Dr. R. N. LACY asked if the assumption that the ratio of nitric oxide to nitrous oxide was constant was a valid one, and whether the effect of variation of that ratio on explosion limits had been studied.

Dr. DERBYSHIRE said that the ratio of nitric oxide to nitrous oxide only remained constant if the buffer tanks were being fed from a number of autoclaves. If the gas from only one autoclave were passed to the buffer tanks then the ratio of nitric oxide to nitrous oxide varied considerably. The limits of flammability of *p*-xylene in mixtures of nitrogen oxides did depend very markedly on the ratio of nitric oxide to nitrous oxide but this had been taken into account in defining the safe maximum amount of *p*-xylene in the gas entering the buffer tank.

Dr. S. A. MILLER referred to Dr. Derbyshire's study of a flammability of the hydrocarbon vapours in various mixtures of nitrous and nitric oxides. He asked whether this had confirmed that flammability was markedly greater in nitrous oxide than in nitric oxide.

Dr. DERBYSHIRE replied that it was.

Mr. A. P. OELE asked if it would contribute to the safety of the condensing system if Raschig rings were used as packing for the parts with a big cross-section.

Dr. DERBYSHIRE replied that it would be difficult to do that since the amount of gas evolved during the oxidation was extremely large and that the consequent pressure drop across such a packed condenser would be tremendous.

Mr. D. M. ELLIOTT said that Dr. Derbyshire had intimated that the bursting discs were fitted on the condenser. From papers given earlier in the symposium, it would appear that if the source of ignition were in the reactor, bursting discs ought to be fitted on the reactor.

Dr. DERBYSHIRE replied that bursting discs were fitted to the reactor as well as to the condenser.

Mr. R. J. KINGSLEY said that it seemed a safe assumption that the work reported by Burgyone, Bett, and Muir had been initiated to get more data on the safe use of ethylene oxide under reaction conditions. He imagined that the work presented would cause some of them to think again about plants they were designing or had designed. Did Dr. Burgoyne think that a review was also required of the conditions under which ethylene oxide was stored? He thought that the conditions deduced from the earlier work were that 35 mole % nitrogen was a satisfactory concentration and he believed that some people now worked with concentrations right up to that value. The work presented did not, perhaps, cover storage conditions but it might be possible to make some prediction. Storage temperatures might be as high as 30° C, with an ethylene oxide pressure of 30 lb/in² abs.

Dr. BURGOYNE said that their results indicated that with ethylene oxide at 30 lb/in² abs, a nitrogen content of 43% was needed to suppress explosibility. A total pressure of some 53 lb/in² abs under nitrogen blanket would therefore be necessary to confer safety in those circumstances.

Dr. F. SJENITZER asked Dr. Burgoyne if he agreed that, in the case of detonation, a bursting disc might be preferable to an explosion valve because of its smaller inertia?

Dr. BURGOYNE agreed with that. The point he had made about the distinction between bursting discs and loaded flaps or valves clearly did not apply to detonation when one had already, as it were, the maximum conditions of explosion propagation, and there was no influence through instability that could lead to any acceleration of the process.

The difference between bursting discs and flaps or valves would be most noticeable with slow explosions. With detonations, inertia would be a particular disadvantage since quick operation would be essential for success. In most detonations, it would be a question whether either type of relief would operate in time to be of any use.

Dr. S. A. MILLER said that he had understood Dr. Burgoyne to say that he did not think that the basic mechanism of the explosive decomposition of ethylene oxide was a chain reaction. That was rather startling because it was contrary to the teaching Dr. Burgoyne normally gave to his students in post-graduate lectures in saying that explosions were chain

reactions. Would Dr. Burgoyne suggest that, at a given moment of time, every molecule of ethylene oxide proceeded to decompose in such a manner as to produce a molecule of methane and half a molecule of ethylene, or must there not be some radical intermediates which were essentially the basis of a chain reaction mechanism.

Dr. BURGOYNE said he had not meant to state that that was not a chain reaction of any kind. What he had intended to say was that he did not know what the detailed mechanism was. They had been talking about the possibility of selecting an inhibitor that would interrupt the reaction in some way. Without a knowledge of the reaction mechanism this seems impossible. Certainly the reaction could not proceed in the molecular manner that Dr. Miller had mentioned and radical intermediates must surely be involved.

Dr. L. COHEN said that he did not want to get involved in an argument on the value of bursting discs compared with loaded flaps but there were a number of points to be considered in designing a pressure relief system. In particular, there was the advantage of the flap over the bursting disc in preventing secondary explosions which were often more severe than primary explosions, particularly with rich mixtures. That effect was due to air being drawn into the vessel, after the initial explosion, which the closing of a loaded flap could prevent. Could Dr. Burgoyne give some guidance on the subject?

Dr. BURGOYNE said that secondary explosion could be an important factor where one had initial explosion either of a fuel-rich combustible mixture, leaving some combustible products inside the vessel, or an explosion such as the ethylene oxide decomposition explosion, which gave nothing but combustible products. With a venting system which allowed air to be drawn in, fresh explosive mixture could be formed which might or might not be more dangerous than that first exploded. It was true that the loaded flap prevented that, but the effect of the reversal of the pressure difference across the flap had to be considered. Would the vessel stand the pressure reversal without collapse?

Mr. Z. W. ROGOWSKI thought that he might throw some light on the maximum pressures obtained with bursting discs and covered vents. He had exploded propane-air mixture in a duct. It was closed near the ignition source and there was a vent on the top of the duct near the end remote from the ignition source. Pressure records obtained with the open vents and vents covered by loosely laid covers showed three peaks. The first was thought to be caused by the inertia of the unburnt gas, the second by the inertia of the vent closure or the inertia of the air outside the duct, and the third by some disturbance to the flame when it was near the vent. With a heavier cover the second peak determined the maximum pressure. With the open vent the maximum pressure was determined by the third peak, which occurred when the flame front was near the vent. When bursting discs were used in smaller ducts, they burst at higher pressures and the maximum pressure was always determined by the maximum bursting pressure of the disc.

Mr. R. J. KINGSLEY asked whether the bursting of a bursting disc could act as a source of ignition. Generally, the conditions downstream of a bursting disc were much more unsafe than those upstream, so that if the disc ruptured for reasons of over-pressure or because of an internal explosion of a rich mixture, the composition downstream of the bursting disc would invariably be explosive. Could the bursting of the disc supply the energy for a secondary explosion?

Dr. BURGOYNE replied that it could; there had been experiments at the Safety in Mines Research Establishment on that point, which showed that the sudden release either of an explosive mixture or of an inflammable gas into air, or of air into an explosive mixture, could all produce ignition. That was primarily due to shock wave effects but there were always suspicions about mechanical effects being involved in connection with the sudden bursting of the disc. Such ignitions occurred in connection with pressures of the order of 1000 rather than 100 lb/in^2. For instance, a sudden release of pure hydrogen into the air had been shown to be liable to result in self-ignition from pressures above 70 to 80 atm.

Mr. E. PENNY said, on the matter of ignition following the operation of a bursting disc, that they had had one unfortunate experience with acetylene-oxygen mixture in a storage vessel used in experimental work, when a bursting disc, which had never been replaced, failed from sheer old age. Although the vessel had been installed in a safe place, the issuing gas ignited and a man had been burned. When the vessel was cut open, it was found to contain a very thin layer of dry powdered rust, and they had the idea that the ejection of this rust with the escaping gas, perhaps impacting on the edges of the aperture, had something to do with the cause of ignition.

The moral was that bursting discs should be maintained and replaced regularly. Another moral was that where there was a bursting disc, one should make sure it was doing a job of work. In the particular vessel, the bursting disc had served no useful purpose. Had there been an explosion in the vessel, the bursting disc could not have relieved it. Therefore, in all plant design, it was very important to try and foresee the consequences of failure of the disc and not simply regard it as a cure-all.

Another trouble they had experienced from time to time was when the engineers set the bursting disc too close to the normal operating pressure. Then they always seemed to be in trouble. Unless the discs were replaced after every second or third run they became tired and ruptured prematurely, and a great deal of time was lost and unnecessary work caused.

They always felt there should be quite a reasonable range between the working pressure, the relief pressure, and the yield pressure. He did not think that bursting discs helped very much in reducing the design strength of normal equipment below the maximum pressures which could arise by explosive decomposition of the contents.

Mr. J. I. KRZYMUSKI said that Dr. Derbyshire had described the precautions taken in the design stage to eliminate hazards. No matter how careful the design, there was an inherent danger to the plant, particularly in the start-up period. Mr. Krzymuski wanted to know what was the philosophy which must apply when an accident happened; what happened then? For instance, when the bursting disc on the condenser burst, with the release of toxic vapours, there was a danger of fire near that place: how could fire fighting proceed when there was lighted acid in the vicinity?

Dr. DERBYSHIRE replied that all the necessary safety precautions were in force, respirators were available, and foam

for fire fighting could be piped to each autoclave and condenser bay. He was not in a position to say more on the subject as he was only on the fringe of this particular aspect of the hazard.

Mr. J. R. Blanco wrote :

Dr. Burgoyne has stated with reference to Table I of the paper by Burgoyne, Bett, and Muir that their results differed from Hess and Tilton's mainly on account of the different ignition sources used. The rate of energy release from the fusion of a Nichrome wire would be considerably greater than that from the heated platinum coil of Hess and Tilton's work. When considering the practical conditions for the safety of storage tanks for liquid ethylene oxide, pressurised with nitrogen, the risk of an internal ignition source arising with energy equivalent to a fusing wire is negligible. Thus there appears to be little reason to depart from Hess and Tilton's recommendations which have been the accepted basis for storage tank conditions.

If there were a severe fire outside the storage tanks liquid ethylene oxide would vaporise and rapidly drive off all the nitrogen diluent through the relief valves. The vapour space would then contain pure ethylene oxide which would inevitably explode when any part of the tank surface became sufficiently hot.

In ethylene oxide reaction systems the danger of ignition by a high energy source may be greater, depending on the reaction conditions and the plant design. However, all the accidental explosions of ethylene oxide vessels which have been described, appear to have been caused by rapid polymerisation due to the catalytic effect of contaminants in the liquid phase. Do the authors of this paper know of any causes where plant explosions could be attributed to thermal decomposition of ethylene oxide vapour?

Messrs. Burgoyne, Bett, and Muir wrote in reply :

The ability of a gas to sustain an explosion flame does not in fact depend on the source of ignition, although of course a particular ignition source may be inadequate to initiate flame in a gas that is capable of sustaining it. We endeavoured in our work to avoid this latter limitation by a preliminary investigation of the adequacy of the source of ignition employed (see Fig. 4, page 32). We fear that Hess and Tilton's sources may not in every case have been adequate in this sense.

Mr. Blanco may be correct in asserting that in storage tanks the risk of an internal ignition source arising with energy equivalent to a fusing wire is negligible. On principle however, we do not think that it is wise to depend for safety upon the absence of all sources of ignition or even any particular kind of source.

So far as storage tanks are concerned, however, practical conclusions drawn from our work may not differ greatly from those arising from the work of Hess and Tilton. Thus, with tanks pressurised with nitrogen to 50 lb/in^2 abs (as is common practice), our results indicate that explosive conditions do not exist in the gas space so long as the liquid ethylene oxide temperature does not exceed about 29° C. This condition may not be difficult to fulfil.

We are glad to say that we have no first-hand knowledge of ethylene oxide reactor explosions from any cause and we do not know with what certainty it has been possible to ascertain the cause of those occasional explosions that have occurred elsewhere.

PAPERS AND DISCUSSION AT THE THIRD SESSION

THE QUENCHING OF FLAME BY PERFORATED SHEETING AND BLOCK FLAME ARRESTERS

By K. N. PALMER, M.A.*

SUMMARY

The performance of flame arresters consisting of metal or polyvinylchloride sheeting or blocks, perforated with circular holes, has been investigated. The arresters were mounted in horizontal tubing systems of various lengths filled with flammable propane/air mixtures which could be ignited either at the open end or at the closed end of the tube. The velocity of the flame that was just quenched by an arrester was directly proportional to the thickness of the arrester and varied inversely with the size of the apertures. No significant differences were found in the flame quenching abilities of brass and polyvinylchloride sheeting, under the conditions of test. A comparison is made between the behaviour of perforated metal and wire gauze arresters. Some theoretical consideration is given to the behaviour of the perforated arresters.

Introduction

Most flame arresters or flame traps consist of a solid matrix containing a group of small narrow passages or apertures through which gases or vapours can flow, but which are intended to be too small for a flame to pass through. Thus as the flame enters the arrester it is subdivided into flamelets, and it is clear that all of these should be quenched if the flame is not to propagate to the other side of the arrester. The various types of flame arrester differ mainly according to how this subdivision is obtained and the number and size of the apertures produced. The more common types of arrester include wire gauzes, perforated sheeting, crimped metal ribbon, sintered metal, and towers packed with pebbles or Raschig rings. The arresters differ considerably in their resistance to gas flow. This resistance is an important consideration because in many industrial applications a flow of gas is required through the arrester, and where the gas is propelled by a fan the maximum pressure drop that can be tolerated across the arrester may be only one or two inches water gauge. Where gas is withdrawn from a cylinder, or is pumped, a much higher pressure drop across the arrester is often permissible.

The types of plant and equipment in which flame arresters are now used cover a wide range, so that a complete classification cannot be attempted. Flame arresters are frequently used in solvent-vapour recovery systems, in the vent pipes of storage tanks for flammable liquids, for preventing flash-back in gases supplied to burners or furnaces, and for preventing ignition from the exhaust of motors working in flammable atmospheres. The performance required of the flame arrester depends on the type of system in which it is installed. It is unusual for the system to be completely enclosed, and to remain enclosed should an explosion occur. It is far more usual for a part of the system to be open to the atmosphere either through a duct opening, or a restricted opening such as a nozzle, or through a vent which opens when the gas pressure changes from the normal working range. If ignition occurs between the opening and the flame arrester then the bulk of the hot explosion products are expelled to the atmosphere and the arrester is required only to quench the flame front. If ignition is between a closed end and the arrester, with the opening on the far side of the arrester, then some of the combustion products are expelled through the arrester, which is required to absorb heat from these products as well as from the flame front. In addition, if the gas mixture is flowing through the arrester, and continues to flow after ignition, a flame can stabilize on the arrester or upstream of it, so that overheating can soon develop. It may be necessary to install a detector near the arrester which can activate a valve to cut off the flow of gas.

In order to specify economic designs for flame arresters, information is required on the relation between the structure of the arrester and its flame quenching properties. Recent reviews have shown that in many cases the available information was insufficient,[1,2] so recent experimental work has concentrated on providing this information. Experiments with wire-gauze arresters[3] showed that the velocity of the flame as it approached the arrester determined whether the flame passed through ; the velocity of the flame that was just quenched by the arrester was related to the size of the mesh of the gauze. Cubbage[4] has studied the behaviour of crimped-ribbon arresters against town gas/air flames propagating at high velocities, up to detonation. The present paper describes tests in which arresters consisting of sheeting and blocks perforated with circular holes were subjected to propane/air explosions. Perforated metal sheeting was used because it is sometimes installed as an alternative to wire-gauze arresters ; some tests were also carried out with perforated polyvinylchloride sheeting to compare the performance of arresters of different thermal properties, although these arresters would not be of practical use due to the ease with which they distort and melt. The perforated-metal block arresters were used to determine the effect of substantially increasing the thickness of the arrester, and also to provide a link in design between the thin perforated sheeting and crimped-ribbon arresters which are much thicker but which have non-circular apertures. The velocities of the flames that perforated sheeting and block arresters can quench have been related to the size of the perforations and the thickness of the arresters.

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Experimental

Material and apparatus

The perforated sheeting was a commercial product and consisted of brass or polyvinylchloride perforated with regularly-spaced circular holes. The holes had square edges and were perpendicular to the surface of the sheet. In all cases except one the pattern of spacing of the holes was Pattern A (see Fig. 1), but in one case Pattern B was used ; details of the dimensions and spacing of the holes are given in Table I. The diameters of the holes were accurate to $\pm 0{\cdot}25\%$ but the accuracy of the spacing distances (*a* and *b*) depended upon the diameter of the hole. With diameters not greater than 0·175 cm the values of *a* and *b* were constant to within $\pm 0{\cdot}5\%$, but with the larger holes the tolerance rose to $\pm 1{\cdot}0\%$. The tabulated values of *a* and *b* are means of at least three determinations. These lengths are respectively the least and the greatest distance between the centres of neighbouring holes, measured at right angles to each other.

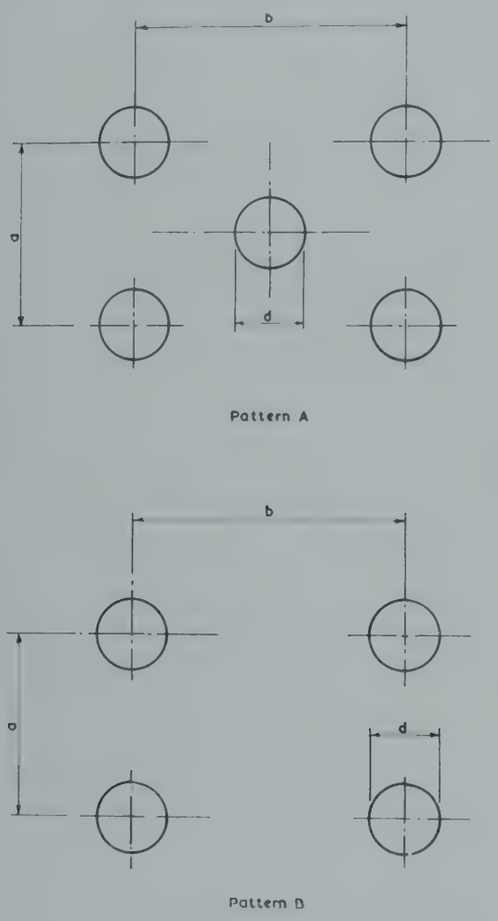


Fig. 1.—*The spacing of the holes in the perforated sheeting and blocks*

A set of perforated blocks was also made in brass with holes of diameter 0·175 cm arranged in the same pattern as the corresponding perforated brass sheeting (Table I). The set of blocks consisted of five units, each 1·00 cm thick and 7·6 cm in diameter, that could be placed in contact so that the holes were accurately aligned.

The tube used for the explosions was mounted horizontally and was made from Perspex, the internal diameter being 6·4 cm and the wall thickness 0·6 cm. The length of the tube and the position of the arrester were changed for different experimental conditions ; details of these arrangements are given in Fig. 2 and in Table II. The wide range of run-ups (distance I–J, Fig. 2) between the igniter and the arrester was used because the velocity of approach of the flame was varied by altering the run-up rather than by changing the gas mixture composition.

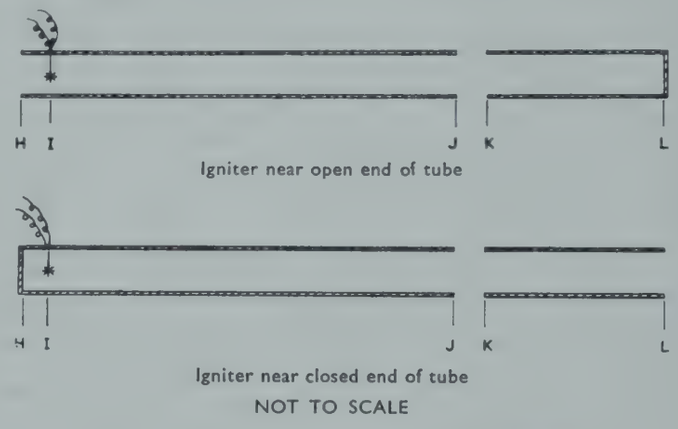


Fig. 2.—*Details of explosion tube arrangement*

The propane used as fuel was specified by the manufacturers as being at least 97% pure ; it was mixed with atmospheric air in the preparation of the explosive gas mixtures.

Measurements of flame velocities near the arrester were made using a rotating drum camera ; the speed of the drum was calibrated electronically by means of a time-period counter. The camera did not photograph the flame directly but *via* two plane mirrors which reflected the top surface of the tube into the camera. The camera lens was focussed at a point 2·1 cm below the interior top surface of the tube (1·1 cm above the axis of the tube). The reason for this arrangement was that when viewed from above in a horizontal tube the flame appears more symmetrical than when viewed from the side. Also, the foremost part of slow flames propagated about a centimetre above the axis of the tube.

Procedure

The arresters were in the form of circular discs or blocks whose diameter equalled that of the outside of the tube.

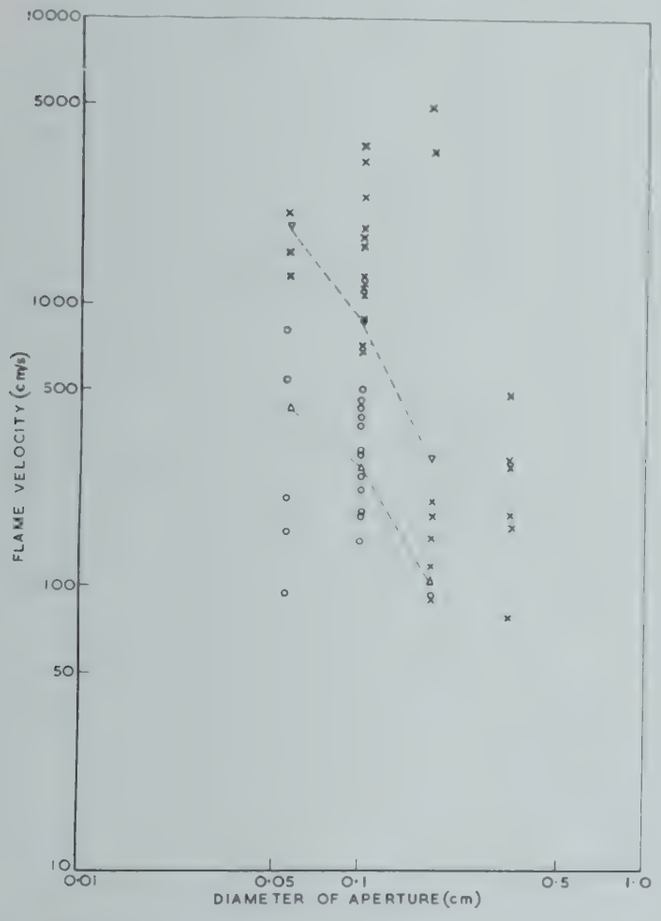
TABLE I.—*Characteristics of the Perforated Brass and Polyvinylchloride Sheeting*

Material	Diameter of hole (*d*) (cm)	Thickness of sheeting (*y*) (cm)	Pattern	*a* (Fig. 1) (cm)	*b* (Fig. 1) (cm)	Area of hole in unit area of sheeting (*P*)
Brass	0·559	0·124	A	0·843	1·42	0·41
,,	0·340	0·118	A	0·442	0·764	0·54
,,	0·175	0·073	A	0·283	0·466	0·37
,,	0·100	0·072	A	0·176	0·291	0·31
,,	0·055	0·046	A	0·112	0·180	0·24
P.V.C.	0·339	0·129	A	0·454	0·793	0·48
,	0·174	0·087	A	0·259	0·450	0·41
,,	0·065	0·059	B	0·149	0·159	0·14

TABLE II.—*Dimensions of Tube Systems used in Centimetres. This Table refers to Fig. 2*

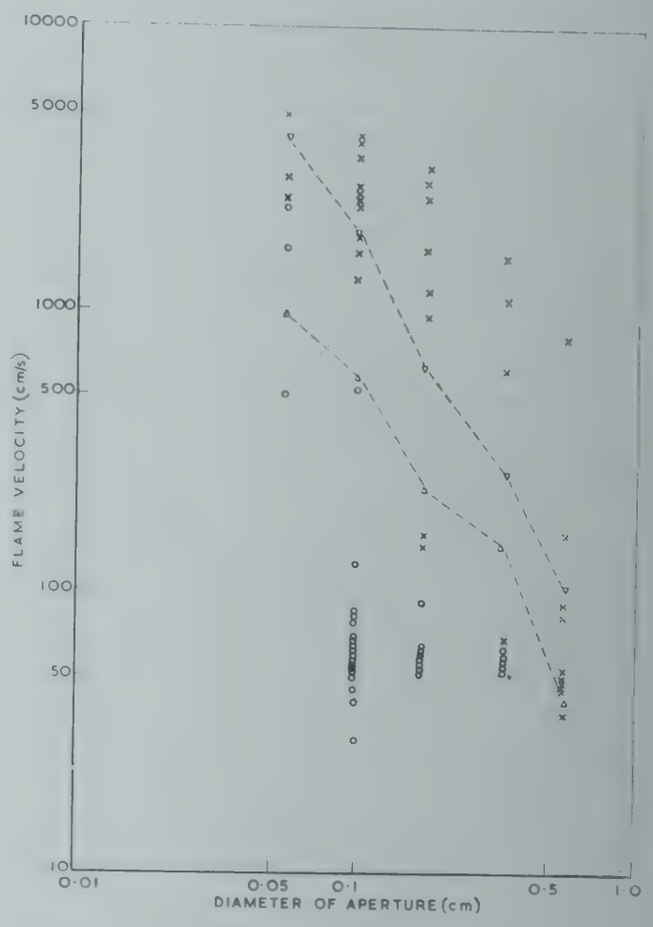
	Arrangement	HI	IJ	KL
Igniter near open end of tube	i	7·6	16·5	63·5
	ii	12·7	34·5	63·5
	iii	12·7	46·0	63·5
	iv	12·7	79·0	63·5
	v	12·7	122	63·5
	vi	12·7	153	63·5
	vii	12·7	305	63·5
	viii	30·5	452	63·5
	ix	30·5	790	231
	x	30·5	1140	262
Igniter near closed end of tube	xi	8·9	11·4	68·5
	xii	7·6	16·5	71·0
	xiii	8·9	34·5	63·5

Before use the arresters were washed in carbon tetrachloride to remove oil and grease, and after drying were inserted in the tube ; the junction between the arrester and the tube was then sealed with transparent tape. The gas mixture was metered through the tube, allowing about ten changes of gas in the tube : the supply was then cut off. The quiescent gas mixture in the tube was ignited by an induction spark from a small coil and the movement of the flame near the arrester recorded by the drum camera. The velocity of the flame was measured at a point 1·5 cm from the arrester on the approach side, although the velocity of approach was usually constant over several centimetres near the arrester. The flame velocity was calculated from measurements of the slope of the flame front on the photographic record and the speed of rotation of the camera drum.



4% propane/air mixtures
Ignition near open end of tube
Tube arrangements (Table II): i-iv, vi
O = Arrester quenched flame
X = Arrester did not quench flame
△▽ = Theoretical points from equations (1) and (2) respectively

Fig. 3.—*The quenching of flames by perforated brass sheeting arresters*

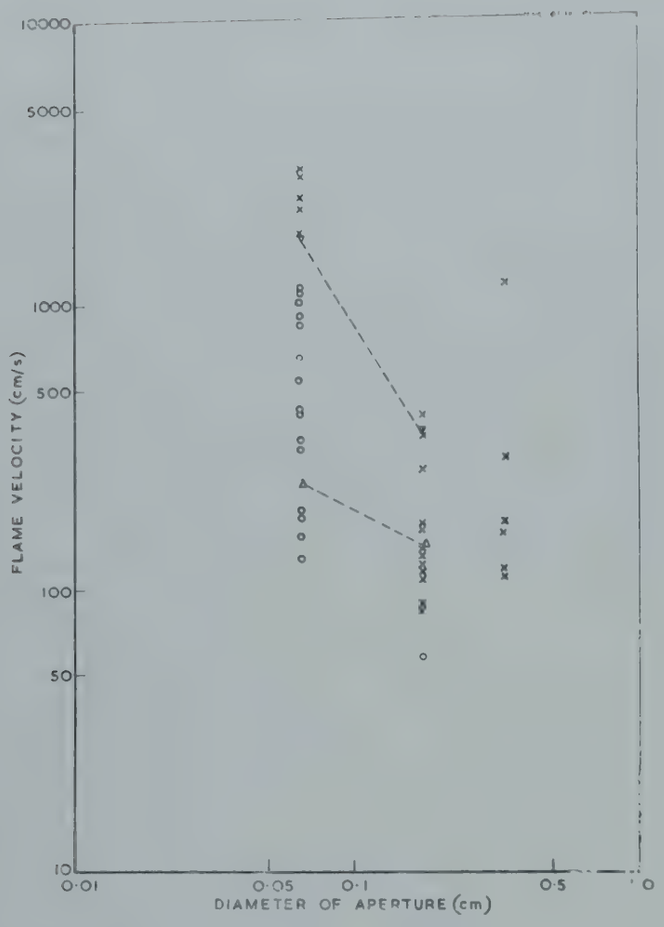


2·75% propane/air mixtures
Ignition near open end of tube
Tube arrangements (Table II) : ii-vii
O = Arrester quenched flame
X = Arrester did not quench flame
△▽ = Theoretical points from equations (1) and (2) respectively

Fig. 4.—*The quenching of flames by perforated brass sheeting arresters*

Results

Two series of tests were carried out with arresters made from perforated brass sheeting and with the igniter near the open end of the tube ; the results for the first series using 4% propane/air mixtures (stoichiometric) are given in Fig. 3. The results for the second series, using 2·75% propane/air mixtures (0·69 × stoichiometric), are given in Fig. 4. In both figures the flame velocity is plotted against the diameter of the aperture on logarithmic scales, and distinction is made as to whether or not the flame passed through the arrester. Details are also given of the various tube lengths used in each series of tests, in general the flame velocity increased as the run-up length (I–J, Fig. 2) was increased, although there was a good deal of overlapping of the flame velocities obtained with neighbouring run-up lengths. The overlapping resulted from the variation in the flame velocity obtained from various tests in a tube of given length. The results of tests carried out under similar conditions with perforated polyvinylchloride arresters are given in Fig. 5. When the polyvinylchloride arresters quenched a flame they appeared to be undamaged,



4% propane/air mixtures
Ignition near open end of tube
Tube arrangements (Table II) : i, iii, iv, vi, vii
O = Arrester quenched flame
X = Arrester did not quench flame
△▽ = Theoretical points from equations (1) and (2) respectively

Fig. 5.—*The quenching of flames by perforated polyvinylchloride sheeting arresters*

as were the perforated brass arresters. However, if the polyvinylchloride arresters failed to quench the flame considerable charring and melting could occur, whereas the brass arresters remained unaffected.

The results of tests with brass block arresters of various thicknesses are shown in Fig. 6, the igniter being situated near the open end of the tube. In all these tests each block was in contact with its neighbours so that the walls of the perforations were continuous through the arrester. The effect of introducing a gap between neighbouring parts of the arrester was also studied. The arrester was built up from two brass blocks separated by a Perspex ring 2·55 cm deep ; this combination was tested in the usual manner, using 4% propane/air flames. The minimum velocity of the flame that could pass through the first block only was about 1000 cm/s. The minimum velocity of the flame required for it to propagate through both blocks was about 1800 cm/s. These velocities are close to the respective values for a single block and for two blocks in contact (Fig. 6) and are in fact slightly lower. It follows that for practical purposes the efficiency of the arrester was not greatly diminished by the introduction of the gap.

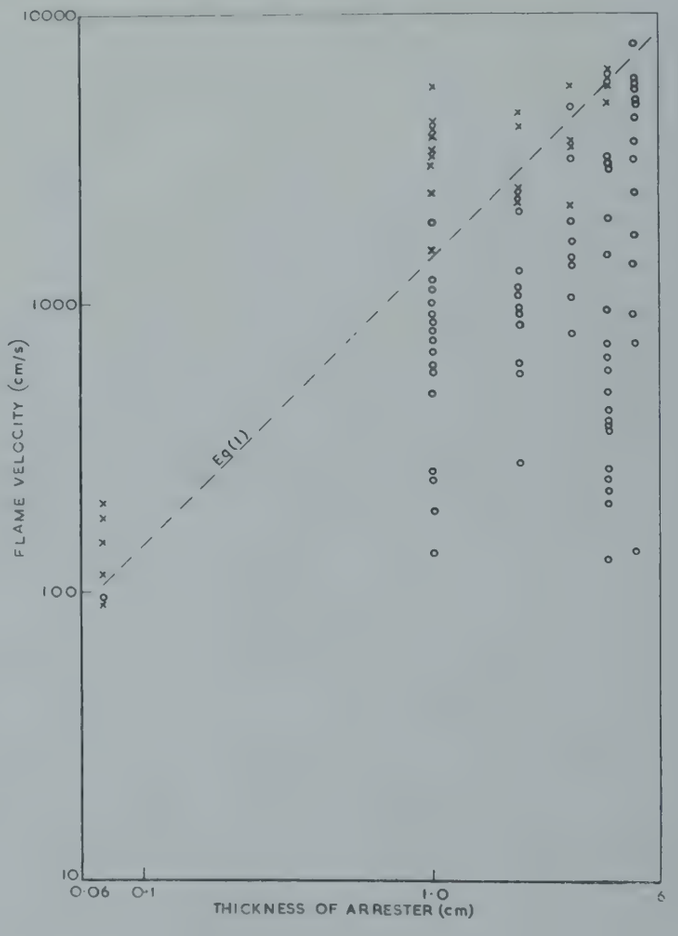
The results obtained with brass block arresters in contact and with the igniter situated near the closed end of the tube are given in Fig. 7. In these tests the gas mixture was streaming through the arrester when the flame arrived, due to expansion caused by the combustion. When the flame reached the arrester its velocity relative to the gas was considerably less than its velocity relative to the tube.

Discussion

Perforated sheeting arresters

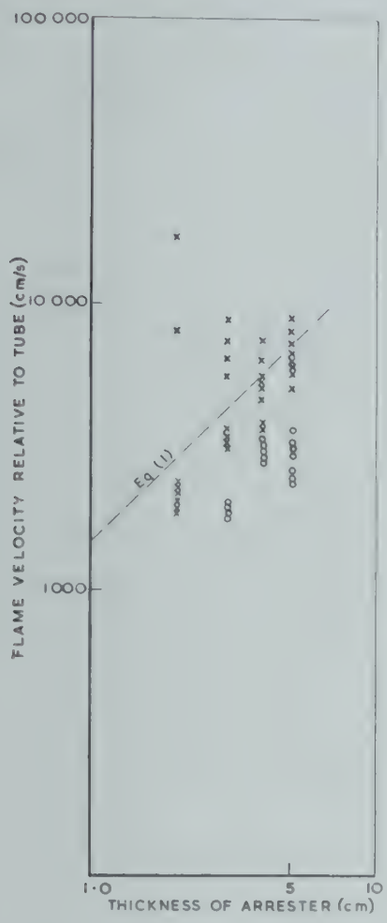
The results for the arresters made from perforated brass and polyvinylchloride sheeting, represented in Figs 3–5, show a clearly-defined dependence of the flame quenching ability of the arrester upon the velocity of approach of the flame. For each size of aperture there was a critical velocity of approach of the flame below which it was quenched by the arrester and above which it passed through. The critical velocity increased as the aperture size diminished. Similar behaviour was found previously with wire-gauze arresters[3] although with gauzes the critical velocity was not quite so clearly defined.

The relation between the velocity of approach of the flame that is just quenched, the diameter of the aperture, and the thickness of the plate is discussed in the Appendix. The argument is similar in principle to that already published for wire-gauze arresters under similar conditions.[3] It is assumed that the quenching of the flame was an effect caused by transfer of heat from the flame to the arrester, so that if more than a certain critical amount of heat were removed the flame would be quenched. The amount of heat removed from the flame by the arrester was calculated in terms of the velocity, tem-



Hole diameter : 0·175 cm
4% propane/air mixtures
Ignition near open end of tube
Tube arrangements (Table II) : iv, vi-x
O = Arrester quenched flame
X = Arrester did not quench flame

Fig. 6.—*The quenching of flames by perforated brass block arresters*



Hole diameter : 0·175 cm
4% propane/air mixtures
Ignition near closed end of tube
Tube arrangements (Table II) : xi-xiii
O = Arrester quenched flame
X = Arrester did not quench flame

Fig. 7.—*The quenching of flames by perforated brass block arresters*

perature and the thickness of the flame, and the dimensions of the arrester. The amount of heat to be removed from the flame for quenching was taken from published results for propane flames on a flat-flame burner. Two conditions were considered : firstly where all the flame front was reckoned to be quenched by the walls in the apertures through the arrester, and none by the blank face of the arrester, and secondly where only that portion of the flame front directly opposed to the aperture was quenched by the walls, the remainder being extinguished at the blank face. In practice the behaviour of the arresters should lie between these two limiting cases ; further discussion is given in the Appendix. The resulting equations are represented by broken lines in Figs 3–5. The broken lines are not always straight because when the diameter of the apertures in the arrester was changed the thickness of the plate also varied (Table I), and the variation was not uniform.

It may be seen from Figs 3–5 that there is fair agreement between the experimental results and the predicted critical values of flame velocities at which the arresters just fail. In each case equation (1) underestimates the critical velocities for arresters with small holes (diameters not more than 0·1 cm), whereas equation (2) tends to overestimate the critical velocities. Equation (1) is in better agreement with experiment when arresters with large apertures are considered, but often the theory overestimates the performance of arresters with large apertures. It is not possible to discern in the experimental results any systematic variation with the material of the arrester, and according to the Appendix none would be expected. As both the thermal conductivities and the thermal diffusivities of brass and polyvinylchloride differ by factors of about 500 any dependence of the flame quenching properties on the thermal properties of the arresters ought to have been detected. Thus, under the experimental conditions, the flame quenching ability of the arrester was probably not governed by the heat transfer properties of the materials of construction of the arrester, but by the rate of transfer of heat to it.

Perforated block arresters

The results for block arresters again show that the velocity of the flame as it approached the arrester is an important factor in determining whether or not it was quenched (Figs 6 and 7). There was a marked increase in the flame quenching ability of the arrester as its thickness was increased. The behaviour of the arresters predicted by equation (1) is represented in Figs 6 and 7 by broken lines. The line in Fig. 6, for flames propagating from the open end of the tube, is in good agreement with experiment over a very wide range of arrester thicknesses.

When the igniter was at the closed end of the tube the unburnt gas ahead of the flame attained high velocities, owing to the expansion caused by the combustion. As a result entrance effects in the apertures through the arrester might become more important, since the inlet length required to set up the boundary layer is proportional to the Reynolds number ; these effects were not considered in the derivation of equations (1) and (2). However, the line calculated from equation (1) is in fair agreement with the results (Fig. 7), although overestimating the efficiency of the arresters, but it predicts that the velocity of the flame that is just quenched should increase linearly with the thickness of the arrester, and this is borne out by the results. In deriving equation (1) it was assumed that the gas flow through the arrester was streamline, although it is of course turbulent in the explosion tube. If the flow through the arrester were taken to be turbulent the velocity of the flame that was just quenched would increase with the fifth power of the thickness of the arrester, whereas the results in Figs 6 and 7 show the velocity to be directly proportional to the thickness of the arrester.

Comparison with wire-gauze arresters

The merits of perforated sheeting and block arresters can be compared with those of wire gauze[3]. With each type of arrester it is the velocity of approach of the flame that is a major factor in determining whether the flame will pass through. As the velocity of the flame depends on the geometry of the duct along which it propagates, this geometry must be taken into account when considering the installation of these arresters. The position of explosion relief vents relative to likely sources of ignition is also important. Both wire gauze and perforated metal sheeting, of the same size of mesh or perforation, have similar effectiveness in acting as flame arresters. These types of arrester are effective only against relatively slowly-moving flames, such as may be generated in short lengths of ducting. Perforated blocks are considerably more effective than sheeting and can be more effective than very fine gauze, which is often ruled out for practical purposes by its high resistance to gas flow and its ease of blockage. For high velocity flames, however, suitable perforated blocks are likely to be impracticable and other

types of arrester, such as crimped-ribbon arresters, should be considered. From the practical point of view there are other factors involved in the choice of arrester ; for instance the mechanical strength, the thermal capacity, and the cheapness of proposed arresters must also be taken into account.

Acknowledgments

Miss J. S. Hall, Mrs. P. M. Hinkley, Mrs. S. E. Stapleton, and Mr. P. S. Tonkin carried out the experiments.

The work described in this paper forms part of the programme of the Joint Fire Research Organization of the Department of Scientific and Industrial Research and Fire Offices' Committee ; the paper is published by permission of the Director of Fire Research.

APPENDIX

The case is considered of a flame propagating along the explosion tube towards an arrester of thickness y perforated with holes of diameter d. The velocity of the flame as it propagates along the tube is the sum of V, the velocity of the flame relative to the gas, and v, the velocity of the gas relative to the tube. In the experiments measurements were made of $(V+v)$. When ignition was at the open end of the tube the assumption was made that owing to the movement of expanded exhaust gases out of the tube, and to the acoustic vibrations excited by the flame, the unburnt gas was slightly compressed ahead of the flame and the motion of the gas was sufficient to establish a boundary layer in the passages through the arrester. When ignition was at the closed end of the tube the gas was streaming rapidly through the arrester when the flame arrived. It may be shown that the flow of the flame gases of 4% propane/air mixtures will be streamline ($Re < 2000$) through apertures 0·175 cm in diameter so long as the velocity of the flame relative to the tube $(V+v)$ is less than 5500 cm/s. Thus about half the results shown in Fig. 7 come in this region and most of the remainder are in the region of transition to turbulent flow. It has been assumed that the flow was streamline, whether the flame originated at the open or at the closed end of the tube and that the boundary layer was fully developed, *i.e.* that entrance effects could be neglected.

Coulson and Richardson[5] considered theoretically the heat transfer between a tube wall at constant temperature and fluid in streamline flow. By using a cubic relation for the radial distribution of temperature in the fluid, the rate of heat transfer at the tube wall was obtained in terms of the axial temperature of the fluid.

The rate of heat transfer per unit area of tube wall would then be :*

$$2{\cdot}4K(T_h-T_o)/d.$$

In the present case if the apertures in the arrester are sufficiently close together for all the flame to be quenched by the walls of the aperture, and none by the blank face of the arrester, then unit area of arrester face corresponds to

$$(4P/\pi d^2)(\pi yd) \text{ area of aperture wall} = 4Py/d.$$

The rate of heat transfer per unit frontal area of arrester is

$$9{\cdot}6KPy(T_h-T_o)/d^2.$$

If the flame is of thickness $x\,(x>y)$ and travels at velocity $(V+v)$ it is in contact with the arrester for a time $x/(V+v)$, so that the total heat transferred to unit area of arrester

$$= q = 9{\cdot}6KPxy(T_h-T_o)/d^2(V+v).$$

The flame front propagates at right angles to itself at the adiabatic burning velocity S, and when the flame front is wrinkled the velocity of propagation along a duct is increased in proportion to the greater surface area of the flame. If the velocity of the flame relative to the gas is V, each square centimetre of arrester is opposed on the average by V/S cm² of flame, *i.e.* $Q = qS/V$. The thickness of the flame, x, is governed by the velocity of the chemical reactions in the flame. If the flame is propagating at velocity V, greater than S, the thickness of the flame is increased by a factor V/S, *i.e.* $x/V = x_o/S$.

$$\text{Thus} \qquad (V+v) = \frac{9{\cdot}6KPy(T_h-T_o)}{d^2\,Q/x_o} \quad . \quad . \quad (1)$$

Equation (1) represents a limiting case in which all the flame front is reckoned to be quenched by the walls in the apertures through the arrester, and none by the blank face of the arrester. In the other limiting case only that portion of the flame front directly opposed to the aperture is quenched by the walls, the remainder being extinguished at the blank face. In practice the conditions for the latter case, in which the apertures are sufficiently widely spaced not to interact, are probably modified since some of the flame front near to the aperture, but not directly opposed, may enter the aperture. The area of flame front to be quenched in the aperture is then larger than the area of cross-section of the aperture. These conditions are intermediate between those for the two limiting cases. When only an area $\pi d^2/4$ of the flame is quenched in each aperture, $P = 1$.

$$(V+v) = \frac{9{\cdot}6Ky(T_h-T_o)}{d^2\,Q/x_o} \quad . \quad . \quad (2)$$

Information is available from various sources on adiabatic flame temperatures and other thermal properties.[3,6–8] The following values were taken for 4% propane/air flames : $T_h = 2000°\text{K}$, $K = 2{\cdot}9\times5{\cdot}8\times10^{-5}$ cal cm^{-1} s^{-1} °K^{-1}, $Q/x_o = 2{\cdot}32\times10^{-2}$ cal/cm³. Corresponding values for 2·75% propane/air flames are : $T_h = 1800°\text{K}$, $K = 2{\cdot}75\times5{\cdot}8\times10^{-5}$ cal cm^{-1} s^{-1} °K^{-1}, $Q/x_o = 8{\cdot}92\times10^{-3}$ cal/cm³.

In both cases $T_o = 290°\text{K}$, and values of P were taken from Table I.

The calculated values of $(V+v)$, the velocity of the flame relative to the tube, are included as broken lines in Figs 3–7. In Figs 3–5, where $(V+v)$ is plotted against d, the lines are not straight because y does not vary regularly with d (Table I).

Symbols Used

a, b = spacing of the apertures in the arresters (Fig. 1).
d = diameter of aperture.
K = thermal conductivity.
P = area of hole in unit area of arrester face.
q = heat absorbed by unit area of arrester.
Q = heat lost by unit area of flame.
S = standard burning velocity.
T_h = mean temperature of flame gases in arrester.
T_o = temperature of the arrester.
v = gas velocity along the explosion tube.
V = flame velocity, relative to the unburnt gas.
x = mean thickness of flame propagating at velocity V.

* *Symbols have the meanings given to them on pp.* 56 *and* 57.

x_o = thickness of flame propagating at burning velocity S.
y = thickness of arrester.

The above quantities may be expressed in any set of consistent units in which force and mass are not defined independently.

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RELIEF OF EXPLOSIONS IN DUCT SYSTEMS

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SUMMARY

The authors describe research work carried out by the Joint Fire Research Organization to determine the amount of relief required for ducts connecting plant items.

The influence of size and siting of relief vents on their ability to reduce maximum pressure and flame speeds of explosions in duct systems are investigated and practical recommendations are made.

Introduction

Ducts are frequently used in industry to convey flammable vapours and gases from one part of a plant to another. Although the main precaution taken against explosions is to ensure that flammable mixtures with air do not occur, it is still possible that by mischance an explosive atmosphere may form and become ignited. If this possibility is accepted, there are two main courses open to a design engineer. The first is that the plant should be built to withstand the maximum pressure of an explosion. For relatively short ducts and most explosive mixtures of the majority of flammable gases with air, this is of the order of 100 lb/in^2 if the initial pressure is atmospheric. However, most flammable gases form certain mixtures with air which can give rise to detonation in a duct system if this is sufficiently long or complicated. Under these conditions, pressures of the order of 1000 lb/in^2 might be reached. The second course is to design the plant in such a manner that the progress of an explosion is kept under control and the resulting pressure is limited to an acceptable maximum. The provision of relief vents is one aspect of this approach. A substantial amount of work[1] has been done to provide design data for relief vents for certain individual items of plant, particularly, for example, drying ovens.[2] There is little information available, however, on the amount of relief required for ducts that may connect items of plant or even for items of plant in the shape of ducts.

To fill this gap, a programme of research is being carried out by the Joint Fire Research Organization. The object of this work is to find the influence of the size and siting of relief vents on their ability to reduce the maximum pressure and flame speeds of gaseous explosions occurring in ducts and to develop practical methods of installing these vents. In practice, duct systems may be extremely complicated and a wide range of flammable gases and vapours may be conveyed in them. To obtain a rational picture of the problem it has been necessary in the first place to confine the experiments to very simple systems, in which the gas is initially stationary. The duct systems reported upon in this paper are thus limited to straight lengths, and to lengths containing a single obstacle in the form of a central orifice, a central strip across the duct, a T piece, or a bend. The flammable component has been limited to either propane or pentane, but these vapours may be considered as having explosive properties typical of a wide range of flammable gases and solvents of industrial importance which have fundamental burning velocities of 1–1·6 ft/s. Some of the results that have been obtained so far are presented below. In spite of the limitations of the experiments, these results allow the formulation of general principles that should guide the provision of explosion relief for duct-shaped vessels and duct systems, and also provide empirical data for the design of this relief which has not before been available.

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Experimental

Apparatus

Experimental explosions were carried out in mild steel ducts of 3 in. and 6 in. in diameter and 1 ft square-section. The ducts were made in flanged sections 6 ft long which could be bolted at the flanges either directly or to include some obstruction. In addition, relief-vent assemblies could be bolted to the ends of the ducts. Some of the sections of the 1 ft square-ducts were flanged at the top also, as indicated in Fig. 1.

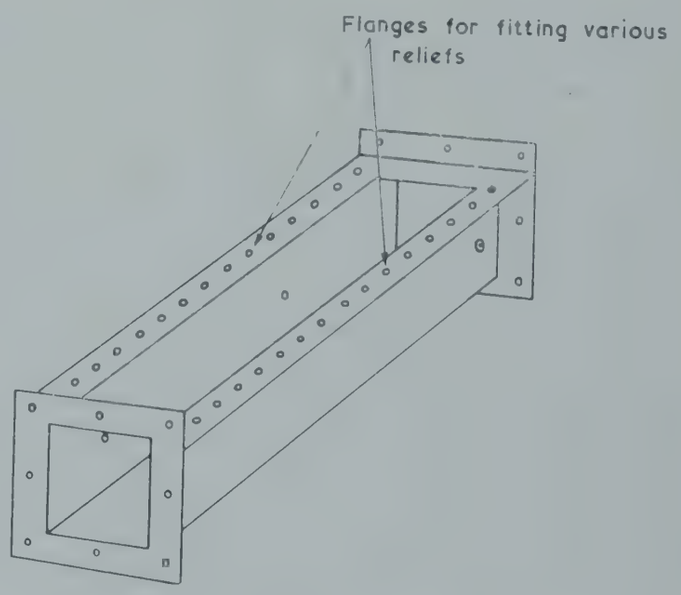


Fig. 1.—*Diagram of 1 ft square duct flanged at top*

These flanges allowed relief vents of various designs and sizes to be fitted at any position on the top of the duct. The circular ducts were Class C (B.S. 806 : 1954) and were tested

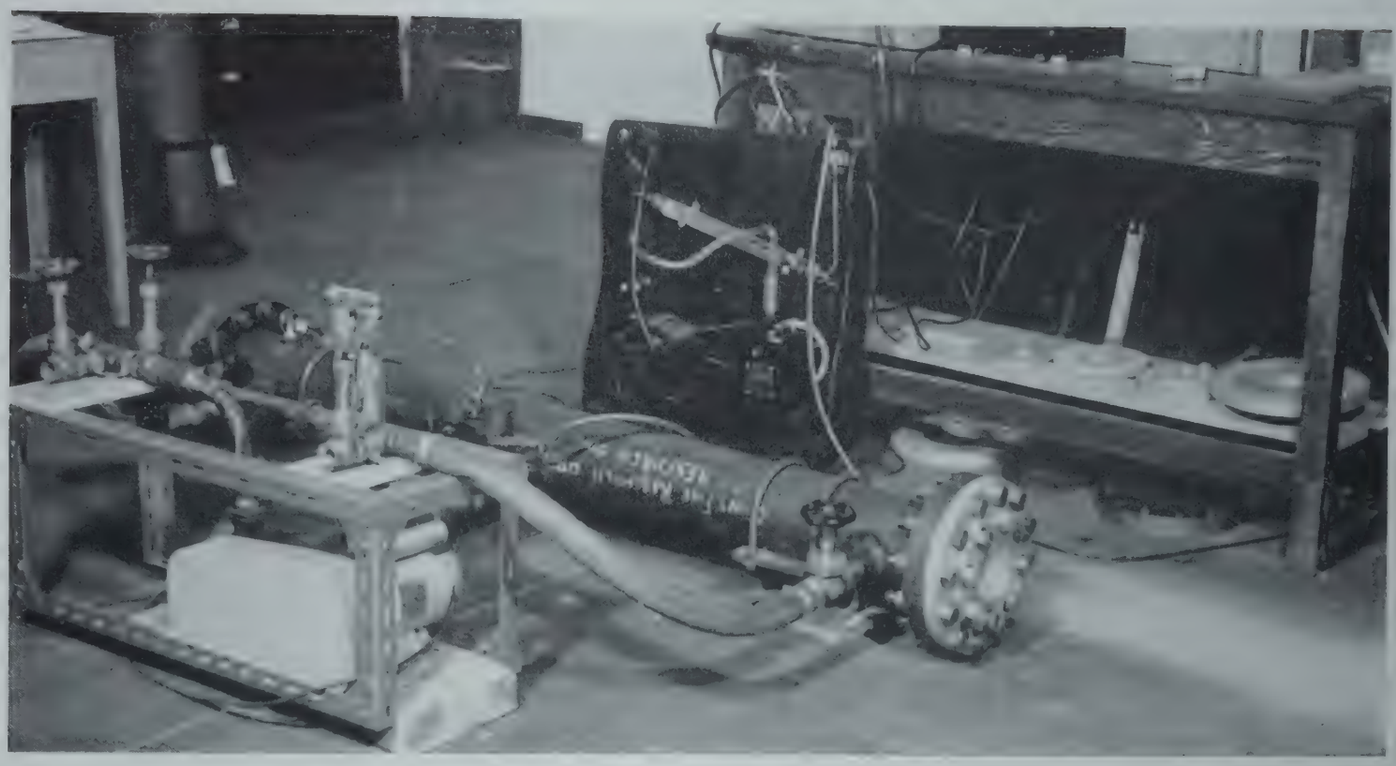


Fig. 2.—*Apparatus using 6 in. diameter duct*

to a pressure of 700 lb/in². The square duct, however, was fabricated from $\frac{1}{8}$-in. steel sheet and could not withstand high pressures. Figs 2 and 3 show respectively a length of 6 in. diameter and 1 ft square duct set up for the experiments. Pentane or propane was the flammable gas. When propane was used, the gas and the air were metered separately and the streams allowed to mix before entering the duct. Sufficient gas mixture to give seven changes was passed through the duct. When pentane was used, the requisite quantity of pentane was introduced into the duct as a vapour and the contents of the duct were circulated with a fan for a time sufficient to ensure thorough mixing. In all tests the gas was allowed to become stationary before igniting the mixture with an induction spark.

Three sets of experiments were carried out :

(1) The effect of end vents in straight ducts was investigated. The three different types of ducts mentioned above were used for this series.

(2) The effect of obstacles placed inside a duct was studied. These experiments were carried out with the 6 in. diameter duct. In most tests, the duct was 12 ft long, closed at one end and open at the other, with the obstacle at the centre. The gas was ignited 6 in. from the closed end. Tests were also carried out to investigate the effect of placing small relief vents in the end near the ignition source, and the effect of increasing the length of duct between the closed end and the obstacle.

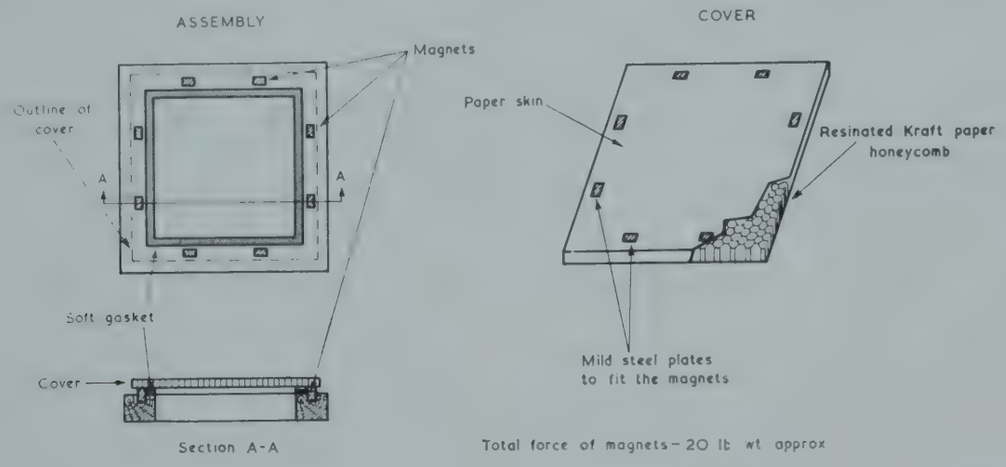
(3) Methods of distributing relief vents along a length of duct were examined. All these experiments were carried out with a 1 ft square duct, the vents being distributed along the top of the duct either as rectangular openings or as longitudinal slots.

Procedure and measurements

In the first two series of experiments, the relief vent at the end of the duct was closed with a bung or cover which was

Fig. 3.—*Apparatus using 1 ft square duct*

removed after charging the duct but before the gas was ignited. In the third series, the vent spaces distributed along the duct were closed at ignition either by loose covers weighing 250 g/ft² of vent area, polythene sheeting 0·001 and 0·0015 in. thick clamped to the edges of the vent, or by light covers weighing 270 g/ft² of vent area clamped to the ducts by magnets. The purpose of the loose covers was to confine the gas mixture in the duct during the interval between charging the duct and ignition, and the results of tests with these covers are the nearest to tests with open vents that could be obtained under the experimental conditions. The two other methods of closure were such as might be used in industrial practice. The magnetically clamped covers were specially designed to give a good seal but nevertheless to be light, robust and capable of being removed at a very early stage in an explosion. Details of their design are given in Fig. 4.



Duct: 12 ft long × 6 in. diameter
Flammable vapour: pentane

Fig. 4.—*Design details of magnetically-held vent closure assembly*

In all experiments measurements were made of the pressure developed during the explosion and of the speed of the flame along the ducts. The experiments with the circular ducts were carried out in the laboratory and a piezo-electric sensing device was used in the measurement of the pressure. The tests with the 1 ft square duct were carried out in the open ; a capacity gauge was used for these experiments since it was less sensitive to the weather than the piezo-electric gauge. In the first series of experiments, the flame speed was measured using ionisation gaps spaced at intervals of approximately 3 ft along the duct and protruding a short distance into the duct. The use of ionisation gaps was found unsuitable for the tests in the second and third series since the obstacles distorted the flame ; the passage of the flame in these tests was, therefore, monitored by infra-red photo-electric cells.

Results

End vents for straight ducts

Details of most of the results of this part of the investigation are being published elsewhere[3] so the results will be only briefly summarised and illustrated here. In correlating the results it was found convenient to express the vent-size as the dimensionless ratio K, equal to the ratio of the cross-sectional area of the duct to the area of the vent. Thus K was equal to 1 and to infinity when the end of the duct was fully open and fully closed respectively. Over a wide range of conditions for both pentane and propane explosions, the maximum pressure when plotted against K fell between the two lines

$$P = 0{\cdot}8K \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and

$$P = 1{\cdot}8K \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where P = maximum pressure in pounds per square inch.

The limits of the conditions referred to above are summarised below :

(*a*) Vent size (K) = 2–32.

(*b*) Ratio of length (L) to hydraulic mean diameter (D) = 6–30.

(*c*) Mixture strength (M) = 1·0–1·3 where M equals the concentration of flammable vapour divided by the concentration in a stoichiometric mixture.

(*d*) Position of ignition source = 6 in. from the closed end of the duct to one quarter of the distance along the length.

(*e*) Position of pressure gauge : any point along the duct.

When ignition took place near the vent, very much lower pressures and flame speeds were obtained than when ignition took place remote from the vent. For example, with a 30 ft length of 1 ft square duct and a vent area of 0·25 ft² (K = 4), the maximum pressure was reduced by a factor of 50 when the gas mixture was ignited close to the vent compared with that obtained with the ignition near the closed end.

Within the limits of equations (1) and (2) there was a complicated inter-relationship between factors (*a*), (*b*), (*c*), and (*d*) above. For example, the concentration at which the maximum pressure was obtained varied with the size of the vent ; this is illustrated in Fig. 5. The position of the ignition source that would give rise to the maximum pressure also varied with the size of the vent. Within the conditions specified, the maximum pressure was approximately independent of the length and the diameter of the duct. This did not apply, however, when the end of the duct was fully open (*i.e.* K = 1). Under these conditions, which are not covered by equations (1) and (2), the maximum pressure was approximately proportional to the length to diameter ratio of the duct and was given by :

$$P = \cdot 07 \quad L/D \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$
$$(6 < L/D > 48)$$

The flame speeds increased as both the length to diameter ratio of the duct and the size of the vent increased. This is illustrated in Fig. 6, which shows the speed of the flame as it approached the vent plotted against the ratio L/D for different sizes of vent. When the end of the duct was fully open, flame speeds of 600–700 ft/s were reached for values of L/D greater than 24.

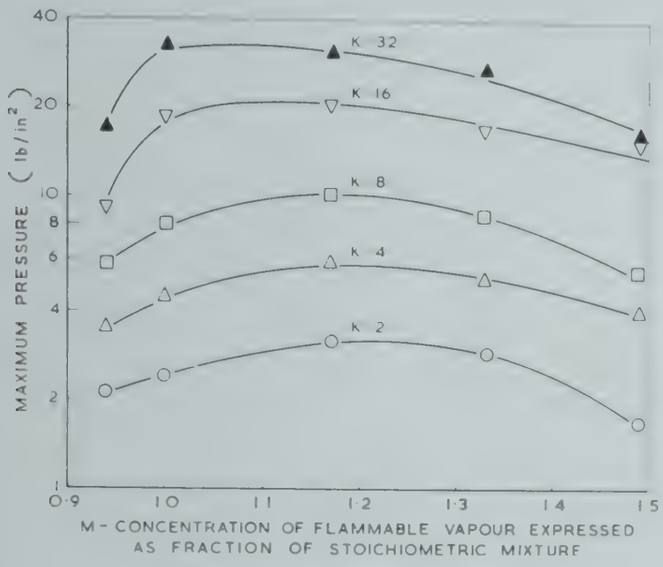

MAXIMUM PRESSURE (lb/in²)
K 32
K 16
K 8
K 4
K 2
M - CONCENTRATION OF FLAMMABLE VAPOUR EXPRESSED AS FRACTION OF STOICHIOMETRIC MIXTURE
Duct 12 ft long × 6 in. diameter
Flammable vapour: pentane

Fig. 5.—*Effect of concentration of flammable vapour on maximum pressure*

The effect of obstacles in the duct

The presence of obstacles in the duct increased the violence of explosions. The effect is illustrated by Fig. 7, which shows a selection of pressure records for these experiments. The flame propagated in a normal manner until it reached the obstacle but immediately downstream of the obstacle there was a rapid rise in pressure. The effect of the nature of the obstacle on the maximum pressure of the explosion is shown in Fig. 8. The maximum pressure was approximately proportional to the resistance to fluid flow caused by the obstacle. A large-radius bend, which did not give a sharp change in the fluid motion in the duct, gave a maximum pressure in the explosion that was less than that caused by the other obstacles of the same resistance to flow. Fig. 9 shows that the presence of the obstacles also gave rise to a sharp increase in the flame speed in the duct downstream from them.

An increase in length of the ducting upstream of the obstacle within the range 3–12 ft did not have a great effect on the maximum pressure reached, although there was evidence, with some of the obstacles of a maximum at a certain length of ducting. (Fig. 10.)

The insertion of a relief vent near the ignition source always brought about a very marked reduction in the maximum pressures and the flame speeds. Fig. 11 shows that broadly similar effects were obtained for different obstacles and different lengths of ducting upstream of the obstacle.

Distributed vents on ducts

EFFECT OF A SINGLE SUPPLEMENTARY VENT

The above work showed that the presence of a relief vent close to the ignition source greatly reduced the maximum pressure and the flame speed. The reason for this effect will be discussed later. It follows that in designing relief vents for duct systems it is desirable to provide reliefs wherever ignition might take place and not only at convenient points in the system. The effect of a supplementary relief vent at different distances from the ignition source was therefore studied in some detail. These experiments were carried out on the 30 ft long 1 ft square duct, the supplementary vent being located in the top of the duct. In all the tests, the duct was fully open at one end, the gas was ignited 6 in. from the closed end and the vent was covered with a light cover weighing 250 g/ft².

Fig. 12 shows the maximum pressure obtained in the explosions plotted against the distance from the ignition source to the supplementary vent, for different sizes of this vent. The maximum pressure increased approximately as the 0·8 power of the distance between the vent and the ignition source, but decreased only as the 0·4 power of the size of the vent. This indicates that for a given amount of venting area, it is better to distribute the area along the duct as small but frequent vents rather than as fewer large vents. Thus, for example, with a venting area of 1 ft² placed 12 ft from the ignition source, the maximum pressure was 1 lb/in². If this vent were subdivided so that there was a vent 0·25 ft² at 3 ft from the ignition source, the maximum pressure would have been 0·6 lb/in.²

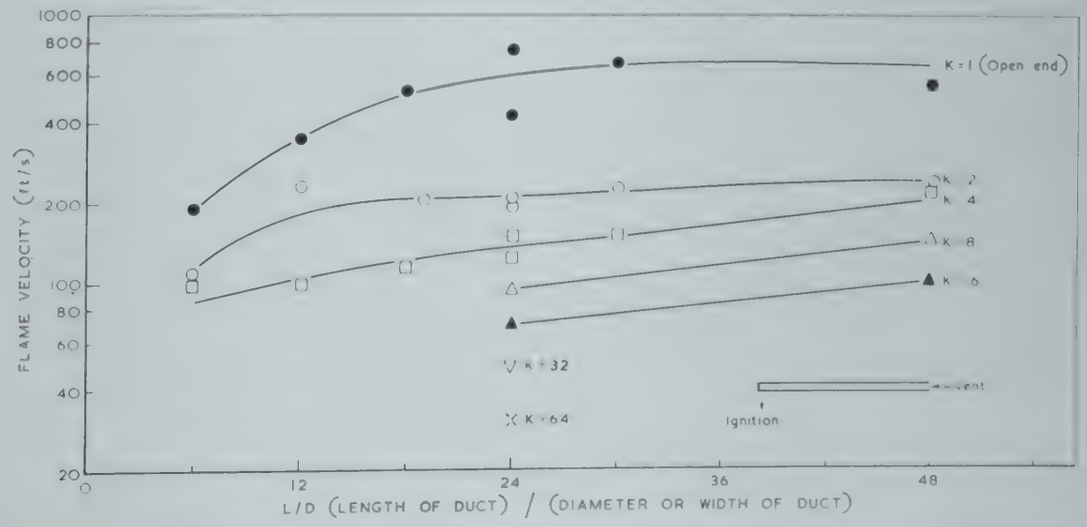
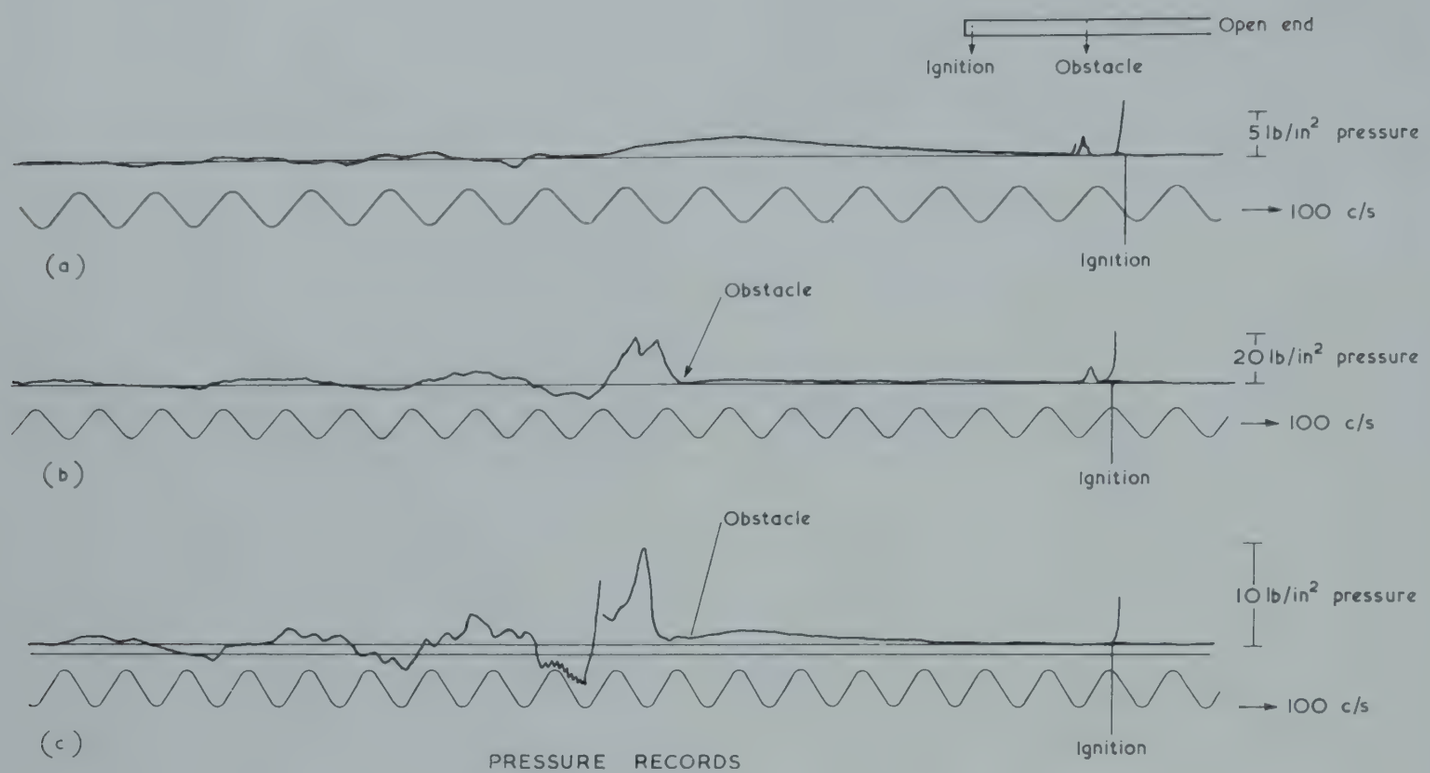


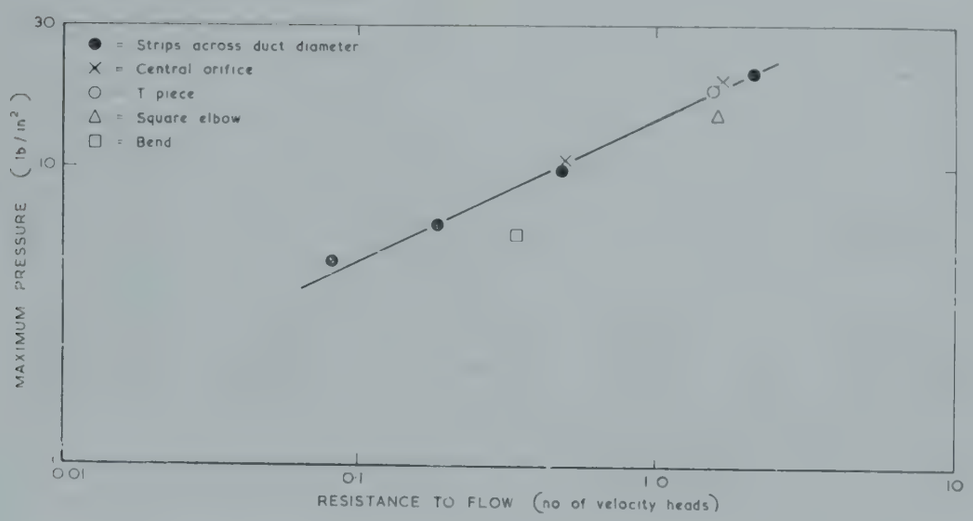
Fig. 6.—*Effect of L/D ratio on speed of flame approaching the vent*



PRESSURE RECORDS

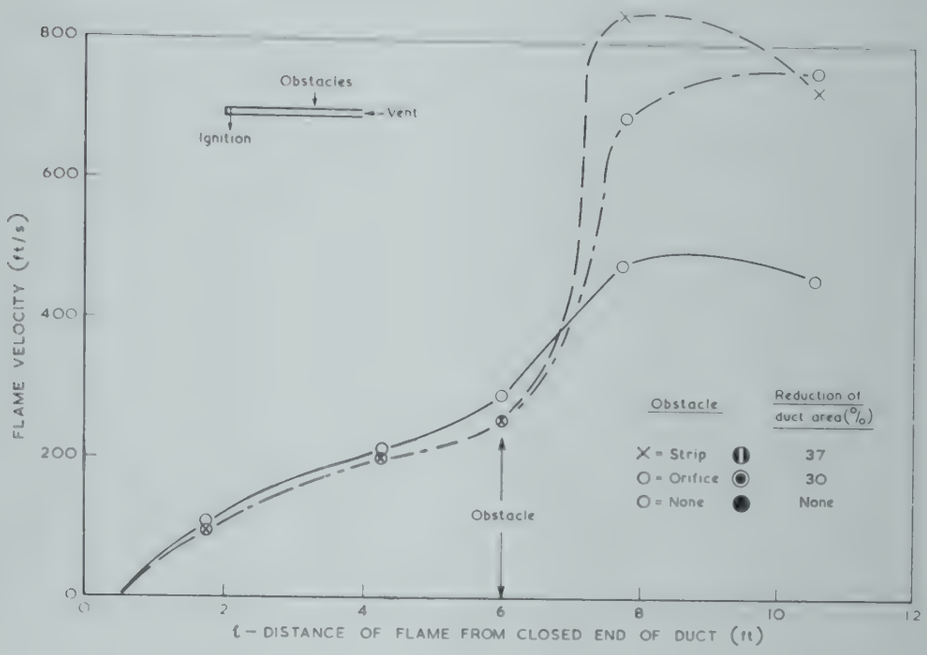
Duct: 12 ft long × 6 in. diameter
Ignition near closed end
(*a*) = no obstacle
(*b*) = obstacle (strip) 37% cross-sectional area of duct obstructed
(*c*) = obstacle (orifice plate) 18.5% cross-sectional area of duct obstructed
Blip on the timing wave indicates arrival of flame front at the probe

Fig. 7.—*Pressure records*



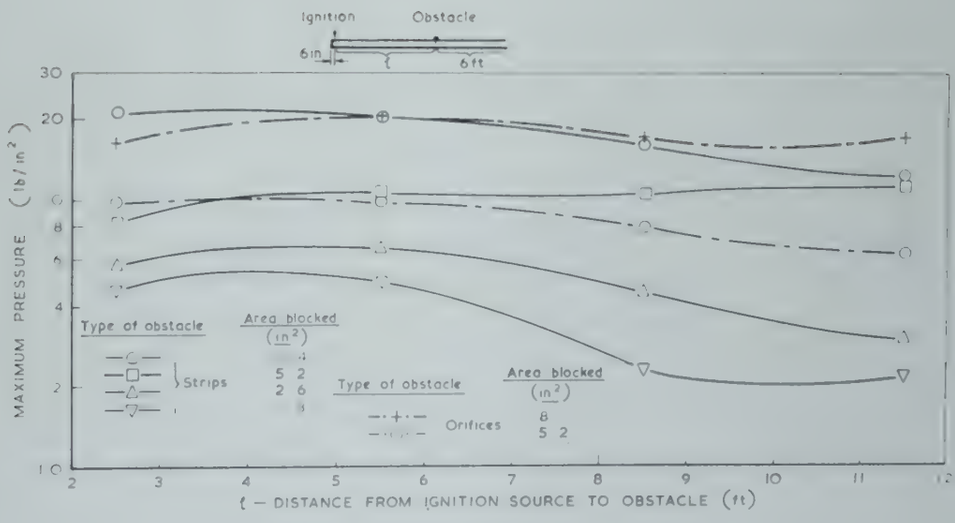
Flammable vapour: propane (M = 1.25)
Duct: 12 ft long × 6 in. diameter. Obstacle in centre

Fig 8.—*Relation between maximum pressure in an explosion in a duct containing an obstacle and the resistance to flow caused by the obstacle*



Flammable vapour: propane (M = 1.25)

Fig. 9.—*Effect of obstacles on flame speed*



Flammable vapour : propane (M = 1.25)

Fig. 10.—*Effect on the maximum pressure of the run up distance to the obstacle*

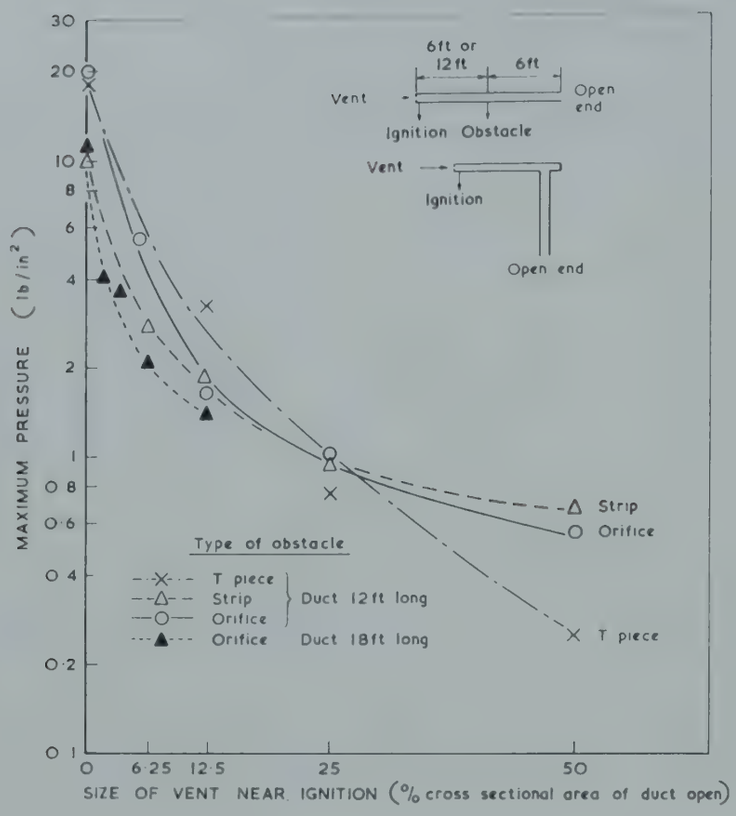
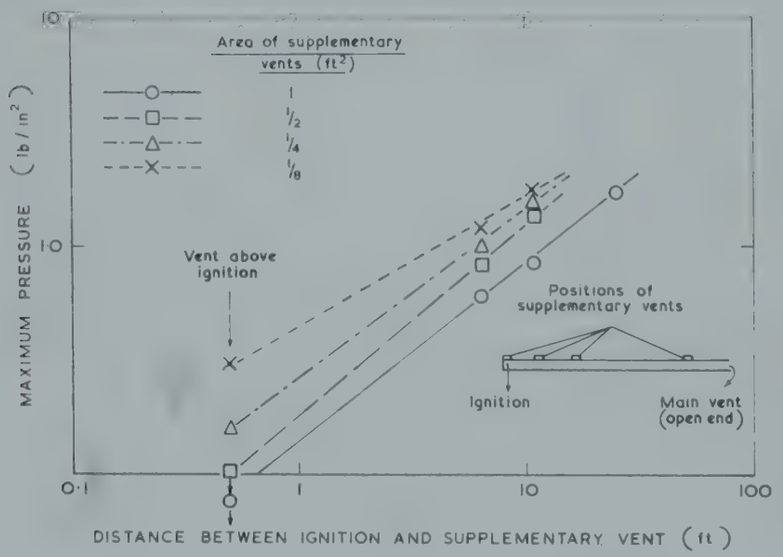
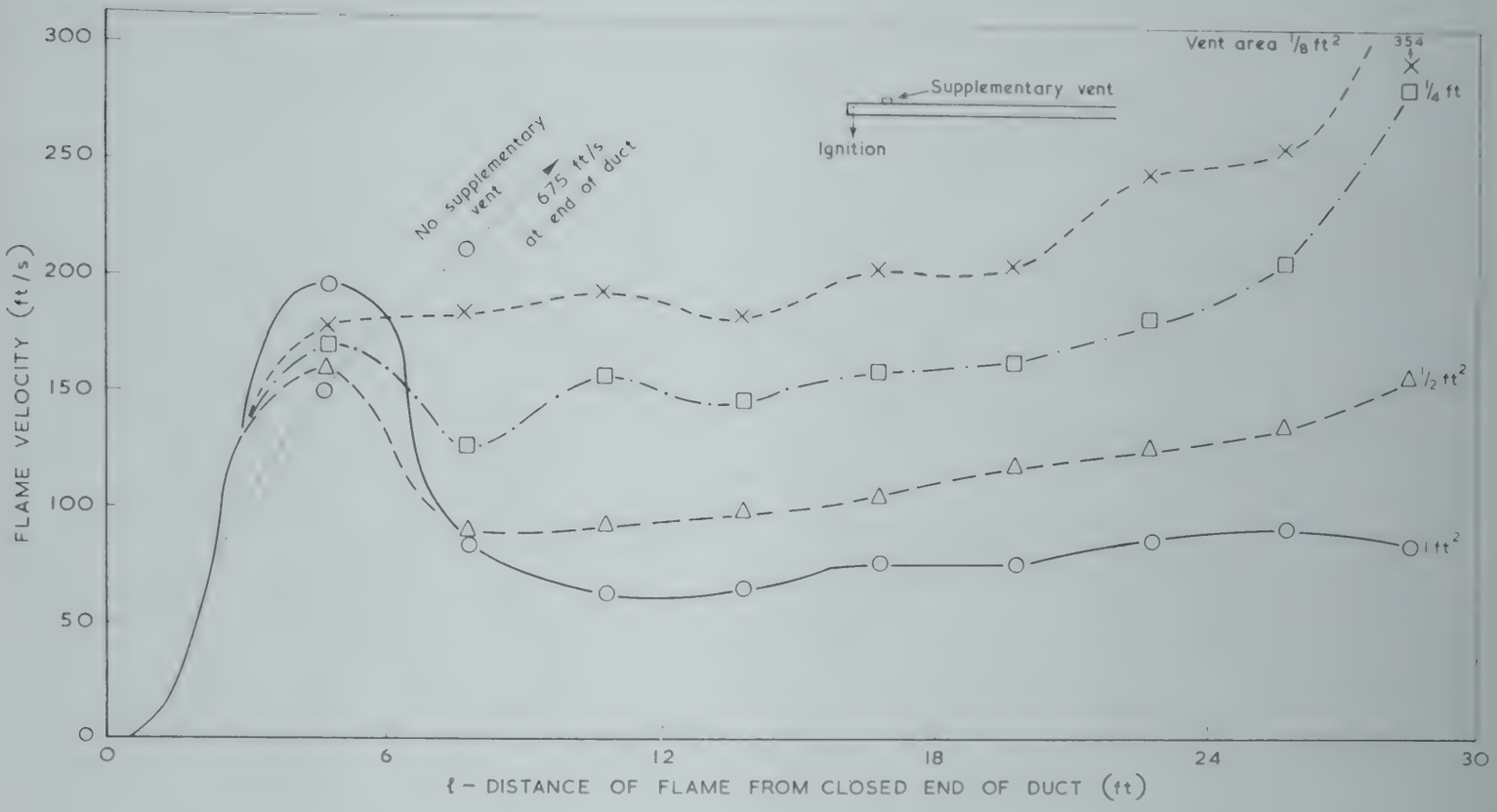


Fig. 11.—*Effect of vent near ignition on maximum pressures for different obstacles*



Duct: 30 ft long × 1 ft square
Flammable vapour: propane (M = 1.25)
↓ Pressure <0.1 lb/in²

Fig. 12.—*Effect of a supplementary vent on the maximum pressure*



Duct: 30 ft long × 1 ft square
Flammable vapour: pentane (M = 1.25)
Vent 6 ft 3 in. from gas source

Fig. 13.—*Effect of a supplementary vent on the flame speed*

Fig. 13 shows the flame speed along the duct plotted against the distance of the flame travel when vents of different sizes were placed 6 ft 3 in. from the source of ignition. The marked reduction in the flame speed as the flame passed the vent is clearly shown, the minimum speed decreasing approximately as the square root of the area of the vent increased.

EFFECT OF A SERIES OF SUPPLEMENTARY VENTS

These experiments were carried out with the main purpose of developing a practicable system of venting a duct containing an obstacle, that would allow maximum pressures during an explosion to be kept down to the order of 1 lb/in². The experiments were all carried out on a 24 ft length of 1 ft square-duct with one end open. The obstacles were installed halfway along the duct, and the gas was ignited at various points between the closed end and the obstacle. Three systems of distributing vents along the duct were studied as follows :

(1) Vents were placed at 6 ft intervals along the duct, one vent being close to the obstacle. The sizes of the vents tested were respectively $\frac{2}{3}$ and 1 ft².

(2) Vents in the form of slots running parallel to the axis of the duct. Each 6 ft length of the duct contained a slot 5 ft long. The width of the slots were 0·8 in., 1·6 in., and 2·4 in., giving respectively $\frac{1}{9}$, $\frac{2}{9}$, and 1 ft² of vent area for each 6 ft run of duct.

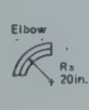
(3) The whole of the side of the duct was constructed to act as a vent. A special duct was made for each experiment by covering a framework of metal rods with polythene 0·001 in. thick.

The maximum pressures obtained in the experiments are shown in Table I, which also shows the method by which the vents were closed in the different experiments. The ducts were too weak for explosions to be carried out with obstacles and without supplementary relief venting. It was estimated that such experiments would have given maximum pressures up to 20–40 lb/in². All pressures shown in Table I are well below this value. The pressures in all experiments with loose covers intended to simulate open vents, were below 1 lb/in². Within this limit, pressures were approximately three times greater when the vents were distributed at 6 ft intervals along the duct than when using vents of equal total area in slot form. It will be noted that when the vents were distributed at 6 ft intervals the flame had to travel 3 ft from the ignition source before it reached a vent, whereas when the vent was in slot form the flame had to travel only 6 in. to the side of the duct. The loose vent covers are impracticable for most conditions likely to be encountered in industry. Replacing these covers by polythene sheet clamped to the duct, or clamping light covers to the duct by magnets, considerably increased the maximum pressure in the explosions. Most pressures, however, remained below 2 lb/in² which is the maximum that can be generally allowed in weak ducts. Relatively high pressures were obtained in some experiments with polythene closures when the gas was ignited close to the obstacle, since the flame reached the obstacle before a sufficient area of the polythene had melted.

Although slot vents were much more efficient than square vents when the vents were closed with loose covers, this advantage was reversed when the vents were closed with polythene.

TABLE I.—*Explosions in a Duct Containing an Obstacle and Provided with Distributed Vents*

Duct—24 ft long × 1 ft square Flammable Vapour—Propane ($M = 1{\cdot}25$)

Venting system	Vent closure	Distance ignition to closed end	Maximum Pressure (lb/in²) No Obstacle	Strips Area Blocked (in²) 6·5	13	26	Orifice Plates Area Blocked (in²) 26	42	72	108	T-piece	Elbow 	T-piece
2·4 in wide slots	Loose covers	6 in.	<0·1	<0·1	<0·1	<0·1	<0·1	<0·1	0·11	0·32	0·1	—	—
2·4 in wide slots	Loose covers	9 ft	<0·1	<0·1	<0·1	0·12	<0·1	<0·1	0·11	0·11			
2·4 in wide slots	Polythene 0·001 in thick	6 in.	0·60	0·50	1·05	1·26	0·50	1·18	1·79	1·76	1·03	—	—
2·4 in wide slots	Polythene 0·001 in thick	9 ft	—	—	—	—	0·79	1·79	7·2	—	0·83	—	—
2·4 in wide slots	Polythene 0·0015 in. thick	6 in.	0·92	0·63	1·62	1·96	0·75	2·09	—	—	—	—	—
1·6 in.wide slots	Loose covers	6 in.	<0·1	<0·1	<0·1	0·10	<0·1	<0·1	0·19	—	<0·1	—	—
1·6 in.wide slots	Polythene 0·0010 in.thick	6 in.	0·70	0·65	1·59	1·81	0·64	1·56	2·70	—	—	—	—
0·8 in.wide slots	Loose covers	6 in.	—	<0·1	0·13	0·27	<0·1	0·29	0·81	0·84	0·13	0·10	—
0·8 in.wide slots	Polythene 0·0010 in.thick	6 in.	0·70	0·78	1·59	—	1·29	2·6	—	—	—	—	—
Square 1 ft²	Loose covers	3 ft	<0·1	<0·1	<0·1	0·1	<0·1	<0·1	0·11	0·16	—	—	—
Square 1 ft²	Loose covers	9 ft	<0·1	<0·1	0·18	0·34	<0·1	0·18	0·29	0·35	—	—	—
Square 1 ft²	Polythene 0·0010 in.thick	3 ft	0·31	—	—	0·50	0·28	0·36	—	—	—	—	—
Square 1 ft²	Polythene 0·0010 in.thick	9 ft	0·35	0·26	0·56	0·96	0·50	0·76	2·40	2·50	—	—	—
Rectangle 2⅓ ft²	Loose covers	9 ft	—	<0·1	0·23	0·61	0·17	0·46	0·77	0·55	—	—	—
Rectangle 2⅓ ft²	Polythene 0·0010 in.thick	9 ft	0·52	—	—	—	—	—	—	—	—	—	—
Square 1 ft²	Covers held by Magnets	3 ft	0·10	—	—	—	0·13	0·21	0·27	—	0·10	—	0·38
Square 1 ft²	Covers held Magnets	9 ft	<0·1	—	—	—	—	—	1·94	—	0·13	—	—
Duct made from Polythene	0·0010 in.	6 in.	<0·1	—	—	—	—	< 0·1	—	—	—	—	—

– Not Determined T-piece referred to in this table is a long-sweep T.

This was because the vents opened initially as a result of the action of both pressure and heat on the polythene film. The bursting pressure of the square vents was considerably less than the bursting pressure of the slot vents at a given temperature. This difference more than outweighed the intrinsically greater efficiency of open slot vents as compared with the open square vents. On the other hand, thin polythene is more likely to be a practicable form of covering for slot vents than for square vents. In all experiments with vents clamped by magnets, a vent cover close to the ignition source was removed at a very early stage in the explosion. When there were no obstructions in the duct or when the obstruction was small, some of the other vent covers were not moved as the explosion travelled along the duct. As a result, the time during which flames were projected from the vent near the ignition source was more prolonged than in experiments with loose covers or polythene sheeting ; in the latter experiments hot gases produced by the explosions tended to be expelled evenly along the whole length of the duct. No measurable pressure was obtained in the tests in which the whole duct was fabricated from thin polythene.

Discussion

The principles of relief venting for duct systems

The work described above illustrates certain basic principles of the progress and control of explosions in ducts. The main initial consequence of a gaseous explosion is the heating of the gases passing through the flame to a temperature of the order of 2000°K. The rate at which gas is heated in this way is directly related to the rate of combustion *i.e.* the speed of the flame relative to the unburned gas. During the period immediately following the initiation of a flame in a stationary gas, this speed is a few feet per second. However, if the heated gas is not free to expand through a vent directly, it will quickly establish a local pressure rise that will accelerate the flame and unburned gas ahead of the flame. After a short time the moving unburned gas becomes turbulent and one of the consequences of this turbulence is that the rate of combustion at the flame front is increased. This process results in the continued acceleration of the flame up to very high speeds. Shock waves associated with the acceleration of the flame probably also play a vital part in the eventual transition

from deflagration to detonation. The effect of an obstacle in the duct is to create a local pocket of intense turbulence in the moving unburned gas which brings about a very rapid increase in the rate of combustion. If the gas is initially in rapid motion the initial propagation of flame is also generally faster and, other conditions being constant, a more violent explosion occurs than when the gas is initially stationary.

It follows that, as a general principle, relief vents should be sited so that burned gas close behind a flame is expelled from the vents ; this would minimize the effect of the expansion of this gas on the motion of the unburned gas ahead of the flame. This implies placing a relief vent wherever there is likely to be a source of ignition. For duct systems it also suggests that relief vents should be installed along the whole length of the duct system to cater, firstly for the possibility of ignition at any point in the duct, and secondly for the diminished effect of a single vent as the distance between the flame and the vent increases. It is also necessary that explosion reliefs, particularly those behind and near the flame, should open at a very early stage in the explosion since otherwise high flame speeds and substantial motion in the unburned gas may quickly be established.

Application of results to practical systems

In view of the wide range of different duct systems that may be encountered the data above are necessarily limited in their direct application to practical systems. If the data are taken in conjunction with information given elsewhere,[1, 4, 6, 7] they can provide an indication of the amount of venting required under different conditions. To apply the information, it is necessary to know the maximum pressure that the system can withstand. It is unlikely that many duct systems as used in practice can withstand pressures greater than 1–2 lb/in^2 and relief venting, if it is to be entirely satisfactory, must keep pressures down to this value under the worst conditions likely to be encountered. Indeed, even if the pressure which the duct system can withstand is substantially higher, say 10–20 lb/in^2, it is still desirable, in order to avoid the conditions that might lead to the building up of detonation in long and complicated duct systems, to provide vent systems that will keep the maximum pressures down to 1–2 lb/in^2 and maximum flame speeds down to about 100 ft/s. For short ducts, however, or for long cylindrical vessels of length to diameter ratios less than about 30, the latter consideration will not apply and the relationship given in equations (2) and (3) may be used to calculate venting requirements.

The information in Fig. 12 may be used to provide estimates of the venting requirements for long ducts with an L/D ratio of 50 or greater. Thus, for example, in a duct of 1 ft square cross-section it may be desired to keep the pressure in an explosion down to 1 lb/in^2 by using a series of vents each of area 0·25 ft^2. Fig. 12 indicates that to achieve this a vent should be no further than 6 ft from an ignition source; this implies that the vents should be 12 ft apart. Moreover, the information in Fig. 6 and equation (3) indicates that, within the limits tested, maximum pressures and flame speeds with open ended ducts scale with the L/D ratio of the duct. In the present context of an indefinitely long duct, the duct length L might be regarded as the distance between two vents. If this is accepted, it is permissible to scale the information in Fig. 12 to ducts of cross-sectional area other than 1 ft square provided the cross-sectional area is of the same order.

An estimate for the venting required when there are obstacles in the duct is indicated in Table I. For ducts containing several obstacles as obstructive to flow as T-pieces or orifices obstructing more than 30% of the duct area, it is necessary to provide vents equal to the cross-sectional area of the duct for each duct length equivalent to six diameters.

These statements apply only to stationary gases and for a single-spark ignition source. It is unlikely that gas speeds of the order of 5–10 ft/s will produce a major difference, since unburned gas speeds of the order of 50–100 ft/s are developed after the flame has travelled the distances stipulated above between vents. However, gas speeds of the order of 20 ft/s and upwards might produce substantial effects, and further work should be carried out on this point. The information is applicable to propane and pentane air mixtures. In many systems it has been found that the venting area required is approximately proportional to the fundamental burning velocity.[2, 4] It can therefore be expected that for gases with fundamental burning velocities similar to propane-air mixtures the above estimates will apply. For acetylene and hydrogen-air mixtures, and for mixtures of most flammable gases with oxygen, the venting stipulated above will not be sufficient. For some of these mixtures, a venting area approaching the whole surface area of the duct might be necessary to keep down maximum pressures and flame speeds. This might be achieved either by constructing the whole duct of a material like thin polythene or by arranging for the sides of the duct to be constructed in the form of light panels which are clamped to a skeleton with magnets or held in place by light friction at the edges. The construction of ducts by these methods will of course incur physical disadvantages but it is a logical alternative to the construction of extremely strong ducts for systems which might be subjected to occasional explosions or detonations.

In principle, the best way of distributing a given area of venting is in the form of a slot along the whole length of the duct. Under these conditions a certain amount of venting area will always be very close to a source of ignition wherever this may occur. If the vent is closed by a diaphragm of a given thickness, then the advantage of the greater efficiency of the slot vent compared, for example, with square vents of size equal to the cross-sectional area of the duct, may be offset by the higher pressure required to burst the diaphragm closing the vent. This disadvantage should not apply to closures held in place by springs, weights, magnets, etc., where, for a given restraint on the closure, the pressure required to dislodge the latter would be independent of its shape.

It should be stressed that if vents are to be fully effective they must open at a very early stage in the explosion and before the flame has travelled more than 1–2 ft. If they are opened by pressure it is desirable that they should be opened completely before the pressure of the explosion exceeds $\frac{1}{3}$ lb/in^2. The magnetically clamped covers fulfil this requirement. Vent covers weighing $\frac{1}{3}$ lb/in^2 would not be so effective because the inertia of these covers might prevent their opening until much higher pressures were reached. If the vents are opened by melting this should occur after contact with the flame for about 1/50 s. The thin polythene sheet used in the tests does not quite fulfil this requirement as it melts in about 1/25 s following contact with the flame.

Use of relief vents in conjunction with flame arresters

The use of an adequate amount of relief venting distributed along a duct system not only reduces the maximum pressure of an explosion but also reduces the speeds of both the flames travelling along the duct and the flame and hot combustion products ejected through the vents. The latter reduction facilitates the design of any flame arresters that may be used

either in the duct to prevent propagation of flame from one unit of plant to another, or at the vents to prevent ejection of flame into working spaces. Thus if it can be ensured that flame speeds are kept down to about 40 ft/s, a single layer of 60 mesh gauze would be adequate to stop the flame.[5] Moreover, when well-distributed vents are used, all of which open in the vent of an explosion, the heat capacity, necessary to prevent failure by melting of any flame arrester placed outside the vents during expulsion of hot products, is limited by the small length of duct that each vent serves. On the other hand, a flame arrester placed outside a single vent at the end of a long duct would have to withstand the passage of hot combustion products generated along the whole length of the duct.

Comparison with present practice

It is common practice at the moment for duct systems carrying flammable vapours and gases to have no relief vent at all. Occasionally, however, relief vents are placed at a number of bends in the duct work; these reliefs are usually closed with discs that burst at 2–3 lb/in². The amount of venting specified in this paper is far greater but this does not imply that such relief vent systems as are now in use have no value. Indeed, they might well be adequate for gas mixtures very near the flammability limits or for explosions in very small local pockets of flammable gas mixtures. Such systems cannot, however, rely on the relief vents as a major factor in promoting safety, and reliance must continue to be placed on keeping concentrations of the flammable constituent well outside the flammability range.

Acknowledgment

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Symbols Used

D = hydraulic mean diameter of vessel or duct (ft).

K = ratio $\frac{\text{(cross-sectional area of duct)}}{\text{(area of vent)}}$

L = length of vessel or duct (ft).

M = concentration of flammable vapour present, divided by the concentration in the stoichiometric mixture.

P = maximum pressure (lb/in²).

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THE DESIGN OF EXPLOSION RELIEFS FOR INDUSTRIAL DRYING OVENS

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SUMMARY

The drying of manufactured articles is a very common industrial process and usually involves the evaporation of a flammable solvent in an oven so that there can be the possibility of an explosion. In practice the hazards accompanying this process can be eliminated by an explosion relief. This paper reports an investigation to determine the data required for the design of satisfactory explosion reliefs. Measurements of the pressure developed by explosions in ovens were made over a wide range of conditions, including the effects of the type of solvent, the size and shape of oven, the size, shape and weight of explosion relief, the presence of shelves, the proximity of walls, and some assessment of oven strengths.

On the basis of the results obtained, a procedure is given for the design of explosion reliefs which will remove the danger to personnel and prevent all but minor internal damage to the oven if there is an explosion.

Introduction

The application of paint, lacquer, enamel, etc., to manufactured articles is widely used throughout industry to provide decorative and protective finishes. This process involves drying the painted articles. A common method is by heating in an oven to evaporate the solvent which is then carried away by a stream of air so that further evaporation is encouraged. The solvent is frequently highly flammable and when vaporised may form an explosive mixture with the air stream. If this mixture becomes ignited, a serious explosion could occur. Faulty operation, also, may result in filling an oven with a fuel/air mixture so providing another source of explosion.

Explosions in drying ovens have caused concern for some time to the Factory Department of the Ministry of Labour and National Service. Although most reported incidents involve vapour explosions, and these occur whatever fuel is used to heat the oven, the majority of the ovens are gas-heated, and so an investigation aimed at the prevention of casualties and damage caused by these explosions was undertaken by the Gas Council.

When there is an explosion in an oven the effects depend on the design of the particular oven involved. Drying ovens may be either continuously or batch operated, and are usually referred to as conveyor or box ovens respectively. The Factory Department statistics show that, of the explosions in drying ovens one-third were in conveyor ovens and two-thirds in box ovens, while of the explosions in drying ovens causing fatalities one-sixth were in conveyor ovens and five-sixths in box ovens. It was clear, therefore, that the immediate problem was the protection of box ovens against the effects of explosions.

Conventional box ovens consist of a metal surround to a heated region through which a stream of air can be drawn by either natural or forced convection. They are usually rectangular in section and have doors forming practically the whole of one side. Either direct or indirect firing can be used. Directly fired ovens for low temperature work can be single-cased with no heat insulation ; for higher temperature work, they are double-cased with heat insulation held between the outer case and inner metal lining. The heating in these ovens is normally by bar burners running across the bottom of the oven. In the indirectly fired ovens, usually called treble-cased, the hot combustion products are led through narrow spaces between the outer insulated double wall and an inner metal lining, which forms the third case, so that there is no contact between the flame and vapours formed in the drying process. Figs 1 and 2 represent typical designs for double and treble-cased ovens respectively. There is considerable diver-

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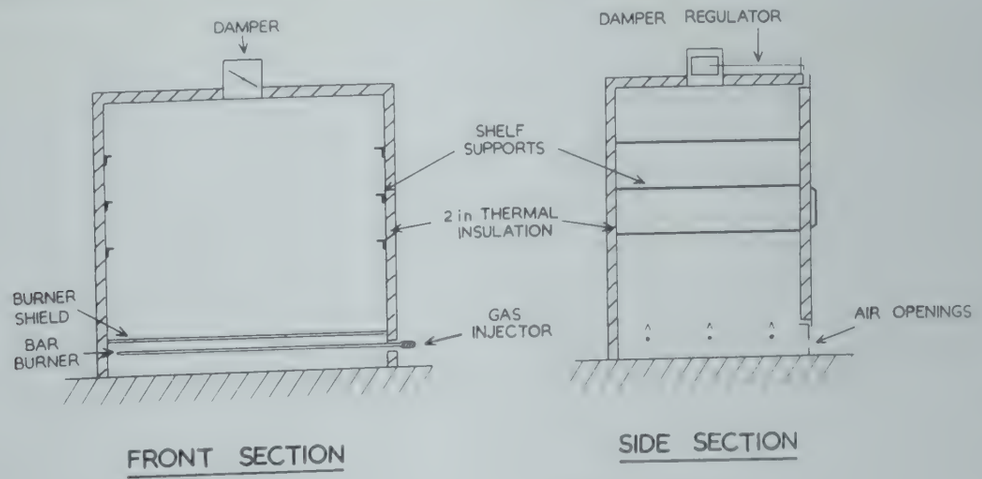


Fig. 1.—*Sections of a typical double-cased oven*

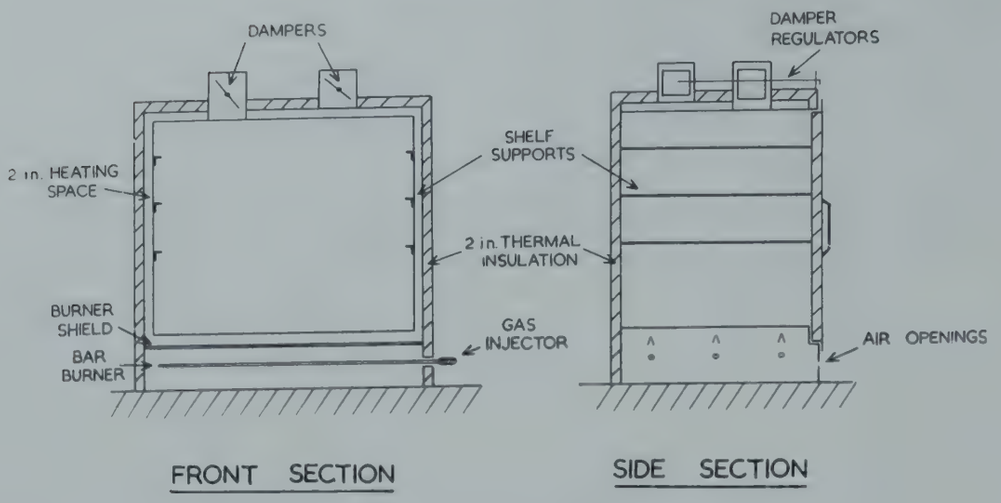


Fig. 2.—*Sections of a typical treble-cased oven*

sity both in the design and size of these ovens for although specialist firms make ovens of a standard size, as advertised in catalogues, particular sizes are made to order, and it is possible for the user to construct his own ovens.

When considering damage due to explosions, the size of an oven is best defined by the volume of the enclosed space in which an explosion can occur. Assessed on this basis the sizes of ovens normally range from about 10 ft^3–600 ft^3. Box ovens are generally approximately cubical in shape, but wide variations do occur.

The damage caused by explosions in these ovens could obviously be prevented either by stopping the explosions or by arranging that explosions could occur without causing damage. Safety devices that would prevent the formation of dangerous concentrations of vapours would be complicated and expensive compared with the cost of a box oven. Attention was consequently directed to relieving the pressure developed by an explosion so that damage was prevented ; this could obviously be done for either vapour or gas explosions by the use of vents to act as explosion reliefs. The provision of explosion reliefs is in fact recommended by the Factory Department.[1] However, there was no direct evidence on which to base the design of such reliefs and the Factory Department was only able to suggest, on the basis of experience, that the area of the vent should be 1 ft^2 for each 15 ft^3 of oven volume, that the relief should be light, that care should be taken to prevent its becoming a dangerous missile after an explosion, and that precautions should be taken to direct the flame and blast away from workpeople.

The urgent requirement was, therefore, to obtain data on which the design of explosion reliefs for box ovens could be based, and this was the object of the investigation reported in this paper.

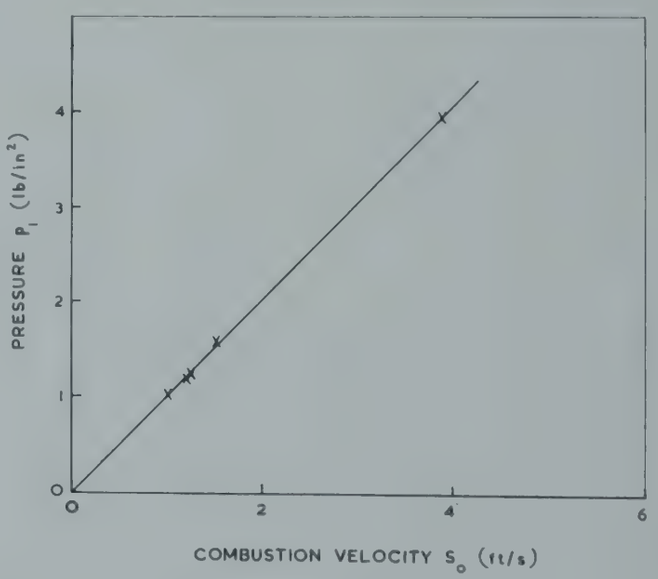
Experimental Results

The general case—empty, cubical ovens

At the start of the investigation very little was known quantitatively about the effect of explosion reliefs on the pressure built up in an oven during an explosion. Furthermore, the size, shape, and construction of the ovens, the drying temperature, the load being processed, and the solvent being evaporated could all very over wide limits. It was decided, therefore, to obtain first some basic information for a general case and then to determine in turn the effect of various departures from the conditions for this case necessary to match industrial working conditions. The empty cubical oven was taken as the general case, and design data for explosion reliefs were determined over a range of oven volumes, vent areas, and weights of explosion relief.

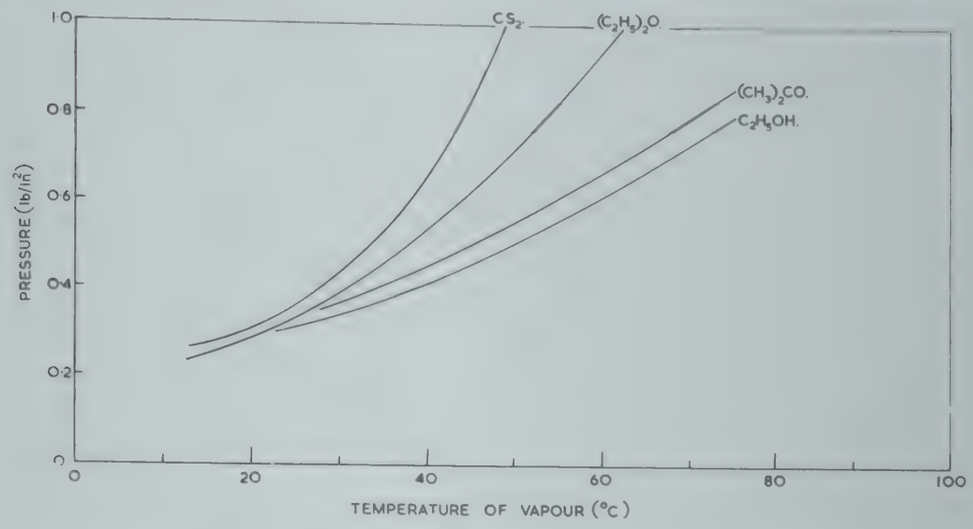
NATURE OF COMBUSTIBLE MIXTURE

Experiments were carried out in which an oven fitted with a relief was filled with a vapour/air mixture which was ignited at the centre of the oven and the pressure developed was measured by a capacity-type gauge inserted in the oven wall and recording on a drum camera. For a number of vapours it was found that the maximum pressure attained for the mixture concentration producing the most severe explosion was proportional to the normal combustion velocity of the mixture as shown in Fig. 3, in which the point for the highest flame speed represents town gas and the vapours are in a bunch at lower speeds. However, if there is an explosion, in practice



Oven volume	= 8 ft^3
Vent area	= 3·2 ft^2
K	= 1·25
Weight of relief	= 4·36 lb/ft^2

Fig. 3.—*Variation of the peak pressure developed by an explosion with the maximum normal combustion velocity of the combustible. In each case the mixture concentration producing the most severe explosion was used*



Oven volume = 48 ft³
K = 1·1
Weight of relief = 1·0 lb/ft²

Fig. 4.—*Variation with temperature of the maximum pressure developed in an oven by explosions of various vapour/air mixtures*

the oven and the vapour/air mixture will be hot; experimental measurements of the increase of pressure generated by an explosion with mixture temperature are shown in Fig. 4.

It was concluded from this that vapour explosions in practice, that is with heated mixtures, produce pressures similar to those obtained with town gas. Most of the experimental work was therefore carried out using town gas since it was quite difficult to fill an oven with a hot vapour/air mixture of accurately controlled proportions. In most cases, the town gas concentration giving the greatest pressure was used.

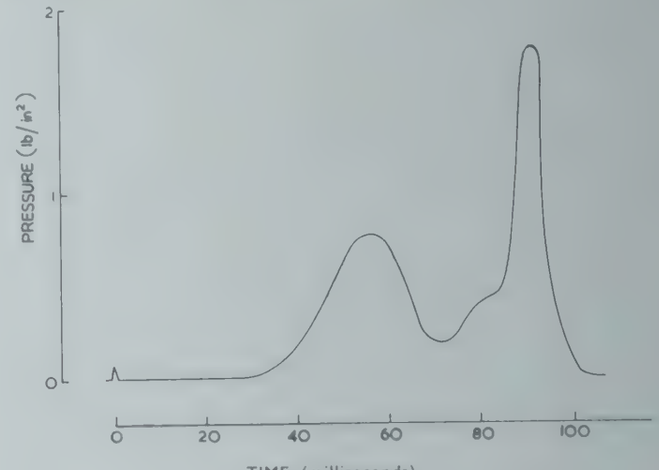
POSITION OF IGNITION

The effect of the position of ignition was studied next and from pressure measurements taken for 17 ignition positions distributed throughout the oven, it was found that the pressure developed was greatest for central ignition, that it decreased slightly as the ignition position was moved away from the centre, and that there was a more marked decrease as the edges were approached. Therefore central ignition was adopted as the standard position in the subsequent work.

VARIATION OF EXPLOSION PRESSURE WITH TIME

For an explosion in an oven fitted with a relief it was found that the variation of pressure with time took a somewhat unexpected form as shown in Fig. 5. This shows a short delay period after ignition, followed by a build up of pressure which eventually becomes rapid, then the relief is ejected and the pressure falls. So far the events are as would be expected. Next, however, there is a sudden rapid rise in pressure followed by a drop to atmospheric pressure.

The origin of the second pressure peak and the shape of the pressure-time curve may be explained by consideration of the course of events in an oven during an explosion. Imagine a flammable mixture ignited at the centre of an oven. Then, as the mixture burns, the volume of the products formed by combustion is much greater than the volume of the mixture before burning, and the pressure inside the oven increases. Ideally, the combustion wave will form a spherical surface centred on the point of ignition. For pressures around atmospheric, the rate of burning is constant and so the rate of formation of products, and consequently, the rate of rise of pressure, depends on the surface area at which combustion can take place. This increases rapidly as the combustion wave spreads outwards and so the pressure rises rapidly until the relief is hurled from the oven and the gases are vented so that the pressure in the oven decreases. Owing to the inertia of the relief, the pressure reached in the oven before the relief is moved far enough for any effective venting to occur is many times the pressure necessary simply to balance the weight of the relief, which is, therefore, projected violently from the oven. The sequence of events does not stop at this point. Combustion is still proceeding in the oven and products are being formed at an ever-increasing pace. It is therefore possible for venting to occur at such a rate of flow that there is an appreciable pressure drop across the vent, and thus a pressure is built up again in the oven. This increases until the combustion wave first reaches the walls of the oven, when the



Oven volume = 98 ft³
Vent area = 9 ft²
Weight of relief = 1·0 lb/ft²

Fig. 5.—*Under these conditions a towns gas explosion would produce a maximum pressure of 0·8 lb/in². Reproduction of a typical photographic record of the variation of pressure with time in an oven during an explosion*

area at which combustion can occur decreases and so the rate of production of products decreases. Thus the pressure inside the oven reaches a second maximum and then falls to atmospheric, so that there is a second peak on the pressure-time curves.

DEPENDENCE OF THE FIRST PEAK PRESSURE ON OVEN VOLUME AND WEIGHT AND AREA OF THE RELIEF

For the general case of an approximately cubical oven using a range of volume and various weights and areas of relief in the top of the oven, it was found possible to correlate the first peak pressure with the oven volume, the weight of the relief and the vent area coefficient. The relation obtained was* :

$$p_1 V^{\frac{1}{3}} = 1{\cdot}18\ \mathrm{Kw} + 1{\cdot}57 \quad . \quad . \quad (1)$$

The agreement of the experimental results with this relation is shown by Fig. 6. The range of oven volume was 8–500 ft³, of relief weights 0·3–7 lb/ft² and of vent area coefficients 1–3.

Some evidence was obtained to show that equation (1) could be expressed in the form :—

$$p_1 V^{\frac{1}{3}} = S_0(0{\cdot}30\ \mathrm{Kw} + 0{\cdot}40).$$

The practical case

The various departures from the general case of an empty cubical oven which are likely to occur under industrial conditions are that the oven may not be cubical, the vent may not be located centrally, and the oven will be loaded or at least contain shelves. The effect of each of these factors was therefore investigated.

EFFECT OF OVEN SHAPE

From the point of view of shape, ovens may be divided into those which have one dimension much greater than the other two and those having all three dimensions of the same order. Ovens in the first category can be considered to be built up of several ovens of the second category placed end to end, and each section can have a suitable relief. The problem thus reduced to determining what range of shapes occurs in the second category. The examination of ovens and catalogues showed that the large majority had dimensions within the ratios 3 : 2 : 1 and 1 : 1 : 1. Experiments with an oven of 100 ft³ volume and dimensions 3 : 2 : 1 gave the results of Table I and showed that whatever side the relief was inserted

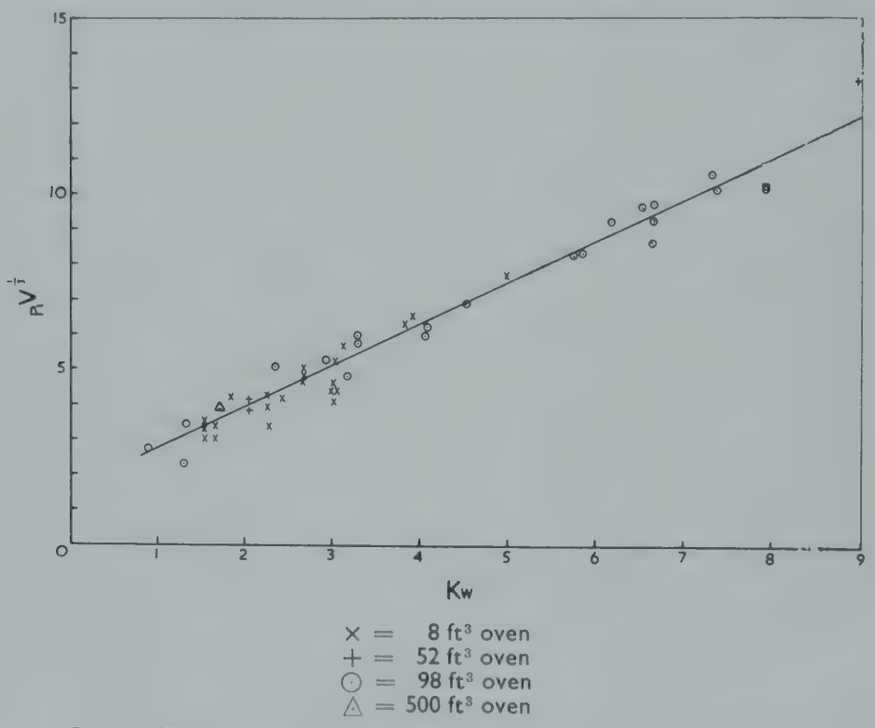


Fig. 6.—*The correlation between first peak (pressure p_1 lb/in²), volume of oven (V ft³), vent area coefficient (K) and weight per unit area of the relief (w lb/ft²)*

DEPENDENCE OF THE SECOND PEAK PRESSURE ON AREA OF THE RELIEF

The variation of second peak pressure p_2 (lb/in²) with the vent area coefficient is shown in Fig. 7 whence it is clear that for design purposes it is reasonable to use a value of p_2 given simply by

$$p_2 = K.$$

In large ovens for values of K greater than 2·5, that is for small vent areas, p_2 increases rather more slowly than given above but, as is shown below, the relation given covers the practical working range.

* *Symbols have the meaning given them on p.* 77.

the first and second peak pressures were always less than those obtained in a cubical oven of the same volume. In these experiments, the weight per unit area of the relief was kept constant and the relief always occupied the whole of the side of the oven.

Thus the design of reliefs could with safety be based on the results for cubical ovens.

EFFECT OF RELIEF SHAPE AND POSITION

It is shown below that the size of a relief must approach that of the oven cross-section in the plane of the relief so that no great variation in shape is possible. However, experiments were carried out with a relief with an area one half of the oven

TABLE I.—*Results of Experiments on 100 ft³ Oven with Shape-factor 3 : 2 : 1*

	Non-cubical Oven			Cubical Oven
	1	2	3	4
Vertical dimension of oven	7 ft 8 in.	5 ft 1 in.	2 ft 7 in.	4 ft 8 in.
Nominal vent area (ft²)	12·5	18·8	37·5	21·0
Oven horizontal cross-section (ft²)	13·3	19·8	39·0	21·0
p_1 (lb/in²)	0·75	0·7	0·3	0·75
p_2 (lb/in²)	1·1	0·85	0·5	1·15

cross section. From these it was found that the explosion pressure was lower when the relief was centrally situated than for any other position. Therefore reliefs should always be located centrally in the sides of ovens.

SHELVES

The presence of shelves and load in an oven would be expected to have a considerable effect on the performance of an explosion relief. The usual type of shelf is a metal grid forming an open mesh.

It was found experimentally that the presence of even one shelf in an oven with a relief in the top caused a great increase of pressure for explosions ignited beneath the shelf (and indeed an appreciable increase for explosions ignited above above it). Unless the fraction of the cross-sectional area occupied by the shelf and load were less than 15%, the pressure became too great for the oven to withstand without some damage. It is therefore essential to use side reliefs for all ovens with shelves. In general this means that the relief must be in the back of the oven since it is then easier to arrange that, if an explosion occurs, the relief is discharged into a region from which personnel are excluded than when the relief is in the side of the oven. Experiments showed that the results already obtained for top reliefs applied directly to back reliefs.

The presence of shelves could affect the performance of a back relief and experiments were carried out to find the effects on the peak pressures of the number of shelves and of the type of shelf, the latter was specified by the degree of blockage that it caused, that is the proportion of the oven cross section occupied by the metal strands comprising the shelf. Some of the results are shown in Figs 8 and 9.

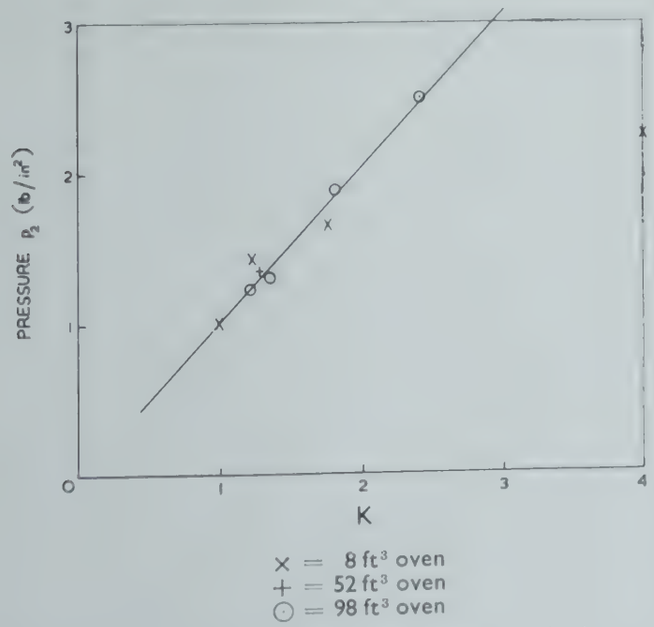


Fig. 7.—*Variation of the second peak pressure with the vent area coefficient*

The general form of each of these curves was predicted by the following arguments. With zero shelf blockage (*i.e.*, with no shelf) the pressure generated is that already known for an empty oven. The effect of inserting a shelf is to promote turbulence in the oven so that explosions are more violent and pressures generated are higher. As the degree of blockage is increased, more turbulence is introduced and higher pressures are produced. However, in the extreme case (*i.e.*, with solid shelves firmly fixed in the oven), the volume of mixture exploding (V) is that contained between two shelves and is only a fraction of the volume exploding when the oven is empty. For such an explosion, the vent area coefficient (K) is unity and the weight per unity area of the relief (w) is the weight of the whole relief divided by the vent area of the compartment in which there is an explosion. Thus the pressure may be calculated from the formula

$$p_1 V^{\frac{1}{3}} = 1{\cdot}18\,Kw + 1{\cdot}57.$$

For example, in a cubical oven of 100 ft³ volume which is fitted with the recommended pattern of relief divided into two equal compartments, the first peak pressure will be 0·65 lb/in² in the complete oven and 0·95 lb/in² in either compartment.

The values plotted in Fig. 8 at 100% metal area were calculated in this manner.

Thus the pressures generated with solid shelves are not greatly in excess of those obtained in the empty oven. Since a shelf was known to cause a marked increase in explosion pressure, it followed that the curve showing the variation of pressure with extent of shelf blockage would rise from the pressure for an empty oven at zero blockage to a maximum as the blockage increases and then decrease again reaching a value for a solid shelf not greatly above the initial pressure with no shelf. The position and height of the maxima were, of course, not predictable. It would also be expected that the effect and, therefore, the maximum pressure would be greater the larger the number of shelves.

On the basis of these results it is recommended that the material of each shelf should occupy at least 50% of the cross-sectional area of the oven. If, with heavy loading, the loaded shelf is virtually solid following this recommendation, lighter shelves should be used and only inserted into the oven when loaded.

SITING OF OVENS—EFFECT OF PROXIMITY OF WALLS

The functioning of a relief is obviously affected by the siting of an oven—particularly by the proximity of walls. Measurements were therefore made of the pressures developed in an oven with a side relief situated at various distances from (*a*) a rear wall, (*b*) rear and side walls or rear wall and floor, and (*c*) rear and side wall and floor. From the results, it was

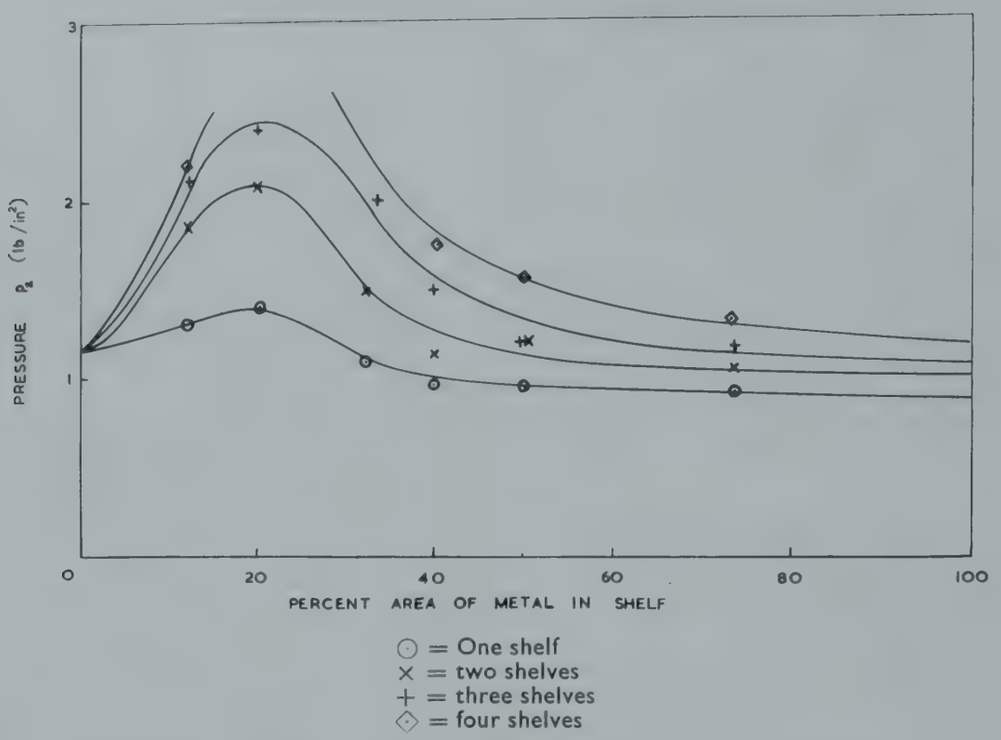


Fig. 8.—*Variation of first peak pressure with shelf area for ovens with back reliefs with 1, 2, 3, or 4 shelves*

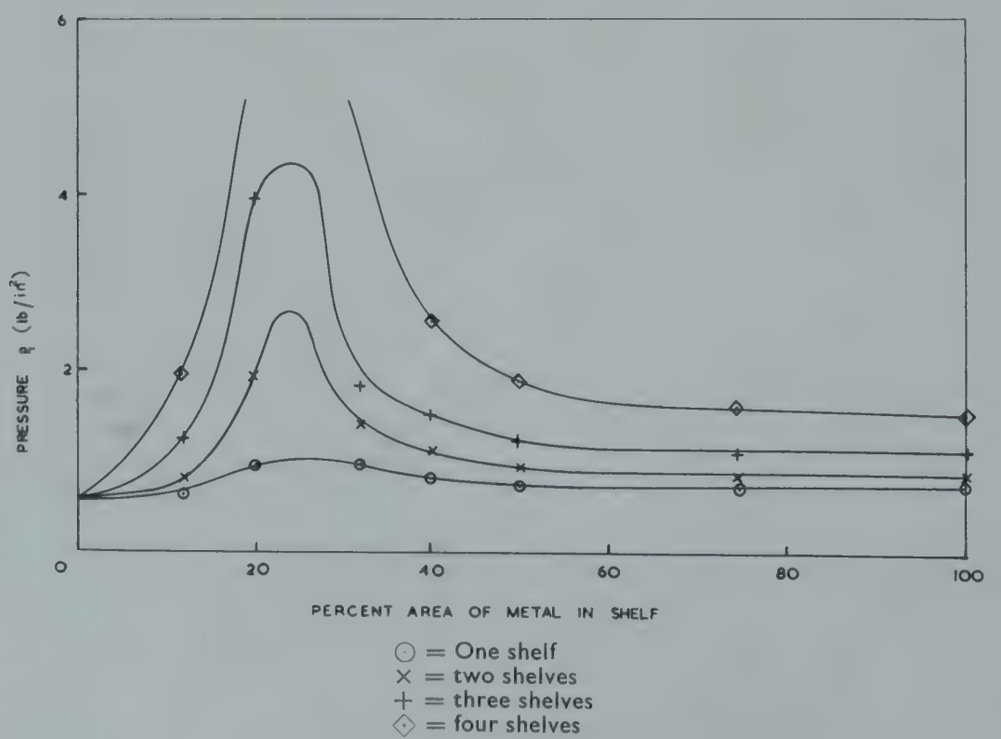


Fig. 9.—*Variation of second peak pressure with shelf area for ovens with back reliefs and with 1, 2, 3, or 4 shelves*

deduced that to prevent a considerable increase in the pressure due to an explosion, an oven should always be spaced at least 15 in. from a wall behind it. If the oven is in a corner, then it should be at least 2 ft from the rear wall and 2 ft from the side wall. Strictly these spacings apply to an oven with a volume of 100 ft³, but since they are relatively modest and vary only as the linear dimensions of the oven, the spacings quoted may be used for ovens with volumes not greater than 150 ft³. For larger sizes the spacings quoted should be scaled by $(V/100)^{\frac{1}{3}}$ where V is the volume of the oven in cubic feet.

The strength of box ovens

For the purpose of designing explosion reliefs the strength of an oven is best specified by the internal pressure that it will withstand. Information on oven strengths is difficult to obtain since it depends on the detailed construction of each oven and moreover it is necessary to test an oven to destruction in order experimentally to determine the pressure it will withstand.

As this work progressed it was found useful to adopt two criteria for oven strengths. These were the pressure below which no damage is caused and above which only minor internal damage occurs, and the pressure below which there is only minor internal damage and above which severe internal damage results. The pressure defined by the latter criterion may be the result of a fairly severe explosion, but since there is no external damage there is no danger to persons in the vicinity of the oven. Both criteria are therefore safe values on which explosion reliefs can be designed.

Experiments have been carried out on three ovens. Two of these were of the normal type using heavy angle-iron and braced sheet metal construction, and the third was the new-style oven of interlocking pressed-steel construction.

The old type, made with a heavy angle-iron frame covered by sheet metal firmly bolted to the framework, is inherently of great strength and rigidity, whereas the new-style oven, constructed from pressed steel sections, is flexible. Because of this, the new style ovens are liable to absorb explosion pressure better than the rigid type of construction which is more liable to disintegrate.

The ovens were all fitted with explosion reliefs. The tests were made at gradually increasing pressures, using centrally ignited explosions of 25% town gas in air mixtures; the pressure variations were obtained by altering the relief weight or by inserting shelves.

Oven A had a volume of 120 ft³ and was double-cased. The doors had an area of 36 ft² and were fastened by an externally mounted bar bolt of $\frac{5}{8}$ in. diameter, which was pivoted centrally. The ends of the bar bolt passed into securing eyes mounted on the main framework.

Oven B was treble-cased and had a working space of 48 ft³. The doors had an area of 25 ft² of which 18 ft² actually covered the working space. The door fastening was of a similar type to that used on the oven described above, but incorporated an additional safety bar.

Oven C was of modern design made from interlocking pressed steel panels, the door bolt being incorporated in the door, which also had a safety bar. The oven was double-cased with a volume of 67 ft³, having doors with an area of 20 ft² and a back relief.

The pressures at which minor and severe damage occurred with the three ovens tested are summarised in Table II.

TABLE II.—*Pressures at which Damage Occurred in Ovens*

Oven	A	B	C
	Pressure (lb/in²)		
Minor Damage	0·75	0·75	3·7
Severe Damage	2·8	3·5	5·0

From these results it is concluded that :—

(1) The new constructional method using lightweight pressed steel sheets resists considerably greater explosion pressure than the old heavy angle-iron type of construction.

(2) For the ovens tested, the maximum pressure that may be allowed to develop is of the order of 3 lb/in² for the usual, rigid type of construction, and 5 lb/in² for the new, flexible type.

It should be emphasised that the evidence on oven strength is still very sparse. The actual strength will depend on the size of the oven amongst other factors. Bearing in mind the fact that most manufacturers use the rigid type of construction, the only possible general conclusion appears to be that oven strengths must not be assumed to be such to withstand explosion pressures above 2·5 lb/in².

The Design of Explosion Reliefs

In designing an explosion relief each of the following requirements must be fulfilled :—

1. The reliefs must be constructed in such a way that they do not form dangerous missiles if explosions occur.

2. The weight of the reliefs must be small in order that the reliefs open fully before the pressure inside can build up to a dangerous level.

3. The areas and positions of the relief openings must be such as to prevent the pressure in the ovens from building up to a dangerous level during the discharge of the products of combustion formed by an explosion.

4. The free space above and around the ovens must be sufficient to allow the reliefs to operate satisfactorily, and attention should be paid to the risk of burns to personnel by the flames discharged from an oven if there is an explosion.

5. The doors of ovens must be provided with secure fastenings; otherwise the doors can fly open in a dangerous manner simultaneously with the operation of the reliefs.

General case—Box ovens

POSITION AND SIZE OF RELIEF

If shelves are used, the relief must be at the back of an oven. The peak pressure developed by an explosion must be safely less than the strength of the oven, *i.e.*, 2·5 lb/in². The pressure developed depends on the weight and area of the relief, the size of the oven, the presence of shelves, and the proximity of walls. Allowing for four shelves and accepting the oven spacing from walls given above, it is necessary to use the whole of the back of an oven for a relief in order to keep the second peak pressure suitably low. With this area of vent and a very light relief which is not dangerous when ejected from the oven, it is found that the first peak pressure is always less than the second, and is therefore safe. Thus, the relief should occupy the whole of the back of an oven.

If the load is suspended from the top of the oven, the relief should be at the back but may be in the top. It is worth noting that it is only rarely that sufficient area is available in the top, and, in fact, one advantage of siting the relief in the back is that the necessary area can be obtained. The only case when a top relief is necessary is the unusual one when the load consists of sheets suspended parallel to the door and substantially covering the cross-section of the oven; the relief should then occupy the whole of the top of the oven.

CONSTRUCTION OF RELIEF

A suitable method of relief construction is illustrated in Figs 10 and 11, the relief being constructed in the following manner.

The basis for this recommendation is the experimental fact that unless such shelves are used there is a considerable increase in pressure if an explosion occurs. It is realised that if the oven is heavily loaded with stock it may not be possible to use the recommended type of shelf since this would cause almost complete blockage. The best procedure in such cases is to use a lighter type of shelf but to insert the loaded shelves after lighting up the oven.

POSITIONING OF OVEN

An oven should always be spaced not less than 15 in. from a wall behind it. [This applies to ovens smaller than approximately 150 ft^3; for large ovens of volume V, the spacing should be $15(V/100)^{\frac{1}{3}}$ in.].

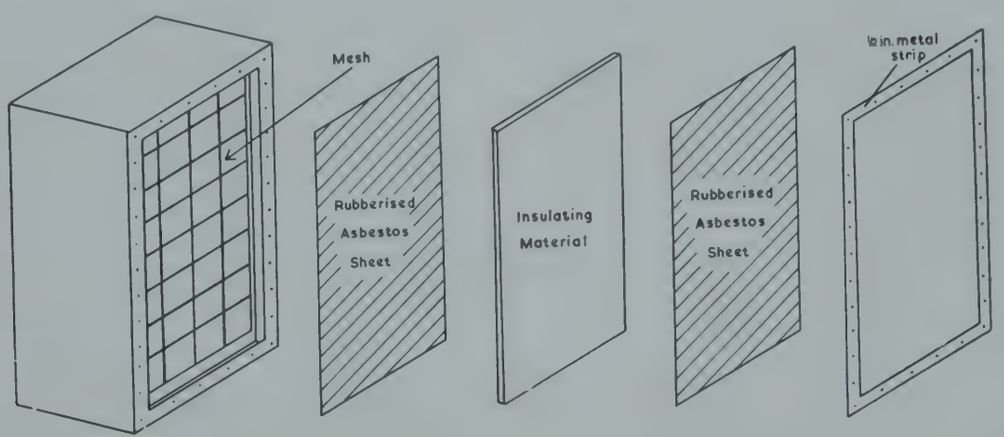


Fig. 10.—*The recommended method of constructing a relief*

The hole in the back of the oven forming the vent is covered by a lightweight metal mesh which is firmly attached to the oven. This mesh should block as little of the area of the vent as possible. A layer of rubberised asbestos, 1/32 in. thick, covers the outside of the mesh and forms a seal. This in turn is covered with a layer of lightweight insulating material such as mineral wool, which is held in place by inserting it about ¼ in. into the double lining of the oven. Finally, this is covered by a layer of rubberised asbestos, which is held in place by ½ in. wide metal strip screwed to the outside of the oven. The screws must on no account pass through or into the rubberised asbestos.

SHELVES

Shelves used in ovens should preferably be made in such a way that the shelf material occupies not less than one half of the shelf area.

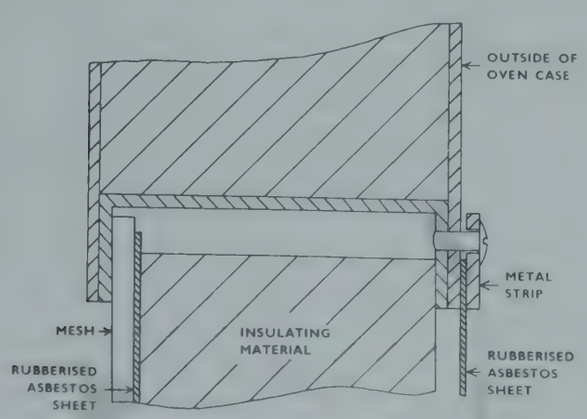


Fig. 11.—*Detail of explosion relief assembly*

If an oven is in a corner, it should be 2 ft from the side wall and 2 ft from the rear wall. [The provision regarding oven volume applies similarly so that the spacing should be $24(V/100)^{\frac{1}{3}}$ in.].

On the few occasions when a top relief is permissible similar recommendations regarding the spacing of the relief from the ceiling must be observed.

PERSONNEL

Precautions should be taken to prevent the entry of personnel to the region into which the relief is discharged and consideration should be given to the risk of operators being burned by flames discharged from an oven.

Special cases

TREBLE-CASED OVENS

The working space of treble-cased ovens may be treated in just the same way as double-cased ovens. Since the relief must be fitted in the back of the oven it is impossible for the heating passages to occupy the back as is the present practice in some ovens.

In treble-cased ovens, the combustion chamber is sealed from the working space and in the larger ovens of this type may be large enough—*i.e.*, greater than 15 ft^3—to require a relief of its own which should be inserted in the back of the combustion space.

LARGE BATCH-TYPE DRYING OVENS

Large batch-type ovens, *e.g.*, core-drying ovens, can give rise to the same kind of explosion risk as box ovens. In fact, the only difference is that of size. The range of size of the experimental ovens was such that it was considered justifiable

to extrapolate the results to volumes as large as this type of oven. Thus reliefs for these large ovens can be dealt with on the same basis as given for box ovens. Because of the nature of the load it may often be permissible to use a top relief with these ovens. In some cases this could ease the constructional difficulties likely to be met with a back relief.

CONVEYOR OVENS

Conveyor ovens usually have approximately square cross-sections but the length is greater than the other dimensions. Any procedure for designing reliefs for conveyor ovens must involve distributing the relief along the length of the oven. It is suggested that the best procedure is to regard them as divided into a number of parts, each of which is approximately cubical, and then to insert a suitable relief into each part. Each of these reliefs can be designed on the basis given above for box ovens.

Conveyor ovens commonly have cross-sections up to about 8 feet square (64 ft^2 area) and so the unit cubes fall in the range of oven volumes experimentally investigated. Although these ovens have open ends, the area of relief provided by the ends is neither large enough nor in the correct position to prevent the oven being damaged by an explosion. Whether the reliefs are inserted in the side or top of the oven will depend on the situation, construction, and loading of the oven.

Practical Verification

Tests on a standard production oven incorporating a back relief designed as specified above showed that the relief limited the pressure to the predicted level and that there was no serious internal damage to the oven and no external effects. It was thus proved that the relief design is satisfactory and a sound production proposition.

It is of interest that an oven manufacturer has independently fitted explosion reliefs to his products following the above procedure and carried out test explosions. No pressure measurements were made but again it was found that there was no serious internal damage and no external effects.

Conclusions

To prevent damage arising from vapour or gas explosions in drying ovens, the following procedure is recommended :—

(1) Explosion relief should be inserted into all ovens, preferably at the back.

(2) The relief should be constructed so that it is harmless and effective. A suitable method is specified.

(3) The relief should occupy the whole of the back of the oven.

(4) Shelves used in ovens should preferably be made in such a way that the shelf material occupies at least one half of the shelf area.

(5) Clearances must always be left between ovens and rear or side walls. Suitable spacings are given.

(6) For treble-cased ovens, the relief (covering the whole of the back) should be divided into two parts that do not connect with each other. One should cover the back of the working chamber and the other the back of the combustion chamber if the volume of this is greater than 15 ft^3.

(7) Precautions should be taken to prevent the entry of personnel to the region into which the relief is discharged.

(8) Consideration should be given to the risk of operators being burned by flames discharged from an oven.

These recommendations apply to box ovens and very large ovens (*e.g.*, core drying ovens). A method of designing reliefs for conveyor ovens is given in the paper.

Acknowledgments

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Symbols Used

A = area of relief (ft^2).
A_1 = area of oven cross-section (ft^2).
K = vent area coefficient ($= A_1/A$).
p_1 = first peak pressure (lb/in^2).
p_2 = second peak pressure (lb/in^2).
S_0 = normal combustion velocity of mixture in oven (ft/s).
V = oven volume (ft^3).
w = weight of relief (lb/ft^2).

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The manuscript of this paper was received on 9 *November*, 1959.

DISCUSSION OF PAPERS PRESENTED AT THE THIRD SESSION

Mr. J. C. MECKLENBURGH said that Simmonds and Cubbage advocated relief at the side of the oven. Derbyshire had put relief at the top on the roof, and Matheson, in presenting his paper, had advocated both methods. Had Simmonds and Cubbage done any work to show which was the best, top or back, or, would they advocate both?

Dr. SIMMONDS replied that work had been done on both top and back reliefs, both of which worked in a very similar way and when properly designed were equally effective. Back-reliefs were preferred for box ovens because of the weight of the top relief and the difficulties of siting a top relief in a box oven.

The top relief had not only to be pushed out of the retaining framework in an exactly similar fashion to the back relief, but it also had to be removed clear of the vent and its own weight opposed that movement. With a back relief gravity assisted the movement and thus a more rapid opening could be achieved. From the practical viewpoint the presence of flues, dampers, damper controls, and fan motors on the top of box ovens split the available area for the relief into a number of small sections and a large proportion of the remainder could be taken up by supports. Another reason for advocating the use of back reliefs was that in the majority of box ovens the work was supported on shelves so that a top relief could be effectively screened from an explosion.

If the work consisted of large sheets that were hung vertically in the oven then, of course, a relief fitted in the top was to be preferred; but that was relatively infrequent and in general back reliefs were advocated.

Dr. F. SJENITZER asked whether a ducted system where there was atmospheric pressure and where vents operated at $\frac{1}{3}$ lb/in^{2}g, could also be used for gases at a pressure of 2–3 atm abs.

Dr. RASBASH said that all the experiments had been made with the contents of the duct at atmospheric pressure. Although it would be expected that the same principles would apply at pressures other than atmospheric, it would become progressively more difficult to put the principles into practice as the pressure inside the duct deviated more from the pressure outside the duct. The values $\frac{1}{3}$ lb/in^2 was a figure to aim at, but good results would be expected if the vent was released at pressure of $\frac{1}{2}$ or 1 lb/in^2 above the pressure in the duct. The difficulty with ducts containing gas at a relatively high pressure—say 30 lb/in^{2}g—would be that even if the vents were arranged to be opened at a slightly higher pressure—say 32 lb/in^2—only the first vent would open efficiently if there was a long series of vents in a duct system. After the first vent had opened the pressure inside the duct might drop rapidly and the differential pressure between the opening of subsequent vents and the pressure inside the duct would be greater than the initial 2 lb/in^2. It was feasible to divide a large duct system into such units by the use of flame arresters. Alternatively, a series of relief vents could be made to open automatically, or the relief vents could be opened by melting on contact with the flame. Thus if polythene were supported on the inside of a wire mesh structure, the pressure which the duct would take before bursting would depend on the closeness of the mesh, but as long as the mesh was not too close it should not interfere with the melting of the polythene.

Dr. SJENITZER said that his question was more concerned with the practical side. If the pressure was 2–3 atm the vents had to be clamped at an excess pressure of more than $\frac{1}{2}$ atm and would become loose at a differential of only $\frac{1}{3}$: that seemed to be difficult to arrange.

There were much stronger modern magnets than those shown in Fig. 2 of the paper by Rasbash and Rogowski wherein there were eight magnets which had to give a total force of 20 lb. There were magnets which were at least 10 times as powerful.

Dr. RASBASH said that there was scope for increasing the differential at which the vents operated. The main thing was to keep the flame speeds down and that was particularly important if ignition took place in the vicinity of obstacles. The pressure differential employed was not limited by the availability of magnets and the usefulness of magnets and similar types of device was that there was little resisting force once the pressure at which the vent began to open was attained.

Mr. J. R. C. CONGDON said that in connection with the magnetically held covers Rasbash and Rogowski mentioned a weight of 50g/ft^2 for the light covers. Could they give a figure for the others?

Dr. RASBASH said that the weights of the covers for both were about 250g/ft^2. The covers held by magnets were clamped to the duct with a force of 20 lb/ft^2, but the weight of the cover was approximately the same as that of the light cover resting on the duct.

Mr. R. H. B. FORSTER said that the application of a polythene duct appeared very attractive but it would be vulnerable to external damage and also might be dangerous to personnel. He enquired whether consideration had been given to the use of a mild steel shield at some distance from the polythene. It would need careful design in order that the venting properties should not be nullified.

Dr. RASBASH said that it would certainly be desirable to have some outside duct to contain the flame as well as to prevent damage to the polythene. They had thought more

on the lines of having a gauze duct outside the polythene duct to act as a flame arrester. The danger of having a closed duct outside the polythene duct was that if there were a leak in the polythene, the duct might become filled with flammable vapour. Also a safe explosion in the polythene duct might give rise to a build-up of unburned gas in the protecting duct which would be followed by a violent explosion.

If the contents of a duct were at approximately atmospheric pressure, the protecting gauze need not be exceedingly fine. Although flame would be ejected in large quantities from the polythene duct in the event of an explosion, the outward velocity would be relatively small and it would be easy to quench. The same consideration might not apply if the contents of the duct were at a high pressure since the bursting of the duct would be followed by a rapid ejection of gas and flame.

Mr. C. A. Cross said he was concerned about what seemed to him to be a slight difference of opinion between the papers by Rasbash and Rogowski and the paper by Simmonds and Cubbage. The first paper advocated the provision of a relief which occupied the whole of the back area of the oven ; when discussing the extrapolation to long ovens, the authors implied that it would be necessary to make the whole of one side of the long oven into a pressure relief. Comparing that with the second paper, on explosions in ducts, quite small relief areas at intervals of several duct diameters were advocated. Was that a discrepancy in the results of the papers or was it due to a difference in the strength that was assumed for the structure?

Dr. Simmonds said one answer was that the sizes of the plants were rather different. The scale considered in the paper by Simmonds and Cubbage was that of the conveyor oven which could have a cross-section of 8–10 ft^2 : that was rather large to be considered as a duct. Rasbash and Rogowski had not experimented with ducts of sizes approaching 8 ft^2 cross-section.

Mr. Cross said that Figs 6 and 8 of the paper by Rasbash and Rogowski indicated that there was a difference in the actual experimental results which might be due to scale effects. In the paper by Simmonds and Cubbage the maximum pressure of 7 lb/in^2 was being developed, with one-quarter the area of vent, whereas in the former paper a pressure of 6 or 7 lb/in^2 was developed.

Dr. Rasbash said that part of the explanation was that the experiment of Simmonds and Cubbage was carried out with town gas and that of Rasbash and Rogowski with propane/air mixtures. There was some evidence that one might be able to extrapolate from a small duct to a large duct. The point was that when the gas was ignited in the middle of the air duct, there were already two vents equal to the cross-section of the duct. The idea of providing vents along the duct was that that system could be maintained. It was an odd way of considering it, perhaps, but the system was different from a cube system. On the other hand, with a duct, there was the opportunity for the flame to accelerate and the combustion rate to be increased if the combustion products were not relieved. With such conditions, a larger venting area was needed. Putting the vents along the duct stopped that happening and allowed the venting present to relieve the gases more efficiently.

Further evidence was also provided by the results of Simmonds and Cubbage with vessels of dimensions $3 \times 2 \times 1$ which indicated that the same correlation employing the K factor could be used both for that vessel and a cube. With the end of the vessel used as a vent, a maximum pressure was obtained which was similar to that obtained when one side of a cube was used as a vent.

Dr. Simmonds said that they had obtained experimentally a difference of about 4 in. pressure between methane/air and town gas/air explosions. Propane has a slightly higher flame speed than methane and thus a difference of a factor of 3 between the pressure generated by propane/air and town gas/air mixtures would be expected.

The explosion pressure increased with temperature of the unburnt mixture and with vapours approaches something very similar to that obtained with cold town gas/air mixtures. Town gas, which was therefore a convenient substitute, was used throughout the experiments.

Mr. R. H. Beresford said that, in the equation presented by Rasbash and Rogowski involving K, one would have to divide by some pressure factor to reduce it to a dimensionless form. Was there any evidence to show that it was related to either the weight per square inch of the cover or to the absolute pressure of the gas? That equation gave a pressure inversely proportional to size of the opening. In the paper it was said that the pressure rise was inversely proportional to the 0·4 power of the size of the opening for supplementary vents. Had the authors any special comments on that?

Dr. Rasbash said that the equation referred to could be made dimensionless by dividing the maximum pressure by the absolute initial pressure in the duct. However, there was not sufficient evidence to say that the equation could then be used for initial pressures other than atmospheric. The weight of the cover could not legitimately be brought into the equation since the results referred to an open vent.

The provision of the supplementary vent gave rise to a substantial alteration in the geometrical disposition of the total venting, extra relief being provided for an explosion which was already relieved by the open end of the duct. In any case over most of the conditions studied, equations (1) and (2) did not apply for K factors less than 2. In the experiments where a supplementary vent was used, the K factor, if it could be estimated at all, was less than 1, though perhaps the K factor ceased to be meaningful under these conditions.

Mr. Beresford said there was no factor of 0·8 except for the supplementary vent. Regarding the size of the vent, Mr. Beresford asked whether the measurement referred to was linear or that of an area.

Dr. Rasbash said that the exponent of 0·4 applied to one supplementary vent at a given distance from the ignition source. The size referred to was the area of the vent.

Mr. A. J. Carter said that he was concerned with protection of ducts which operated above atmospheric pressure. Even if the pressure was only 2 lb/in^2 it was difficult to arrange a vent which would not lift at 2 lb/in^2 but would lift at 2·3 lb/in^2. One required something which would lift when a given rate of change of pressure was exceeded rather than when a given pressure was exceeded. There were such devices but one baulked at the electrical equipment which went

between the sensing element and the vent or explosion suppressing devices.

Dr. RASBASH said that he was not entirely happy with the principle of a relief vent operated by the rate of change of pressure (dp/dt). As indicated by Figs 7 and 10 in his paper, dp/dt could be very small while a flame travelled towards an obstacle in a duct. Downstream from the obstacle there might be a sudden rise in pressure such that even with a vent open quite near by a substantial pressure rise was obtained. The records referred to indicated that if that method were used the detector should operate at a value less than 5–10 lb/in^{2}s within a time of about 1/50–1/20s. He fully realised the difficulty of using the small pressure differential. The only answer was to aim for the smallest practicable differential, though for complete safety there would be an upper limit to the differential which would depend upon the system. Thus examination of Figs 7 and 10 indicated that if it were desired to vent that particular system, the vent would have had to be operated at a differential less than 1–1½ lb/in^2 since that was the maximum pressure prior to the flame reaching the obstacle in the duct.

Mr. V. KENWORTHY said that, as a plant designer, he was concerned with what happened to the relief covers that were removed and secondly, with what was done with the vented products. Ducts were designed in the drawing office to contain noxious vapour, but when an emergency arose another device was needed to deal with the products of explosion. How much must the relief mechanism of ovens be displaced to give the safe pressure relief rate, and how did one accommodate the displaced cover without introducing other hazards? Furthermore, how did one deal with the explosion products released through a large explosion vent inside a plant building?

Dr. SIMMONDS said that the removal of the relief depended on the spacing of the oven from a wall or any other obstacle behind it. Obviously, another piece of plant near the oven was equivalent to a wall. The spacing was the distance to which the relief must be allowed to be projected in order to give sufficient clearance. If the relief were moved only partly out of the way there would be a restriction and a higher pressure generated inside the oven.

In industrial practice, combustion products were not very noxious. They might not be beneficial, but as most of the vapours in the oven would be burnt a highly dangerous atmosphere would not be left. In any case the volume of products released (measured at room temperature) would be relatively small compared with the size of the room in which the oven was installed and thus dilution by the surrounding air would mitigate the problem. The problem would exist, of course, when the vapour being dealt with was a particular hazard itself.

Dr. RASBASH said that the danger that flammable gases and hot combustion products could pour out of a duct system with gases flowing along almost without restriction did give rise to practical objections to the use of relief vents. In theory, one wanted to have everything open to keep the pressure down inside the duct and to keep the flame speed in the duct as low as possible. As far as not allowing more than the absolute minimum of flammable vapours and combustion products to get into the atmosphere was concerned, it might be desirable, after opening, to shut the vents again. It was possible to design relief vents to do that. There were a number of ways in which a vent could open at a very small pressure and, after a while drop back by gravity or springs. It was only when hot combustion products were being pushed out of the duct that the vent was open. It was most important that there should be relief vents in the neighbourhood of the flame—in particular just behind the flame—through which the hot combustion products would leave. It was also important to provide each relief vent with a flame arrester or a gauze, which would at least remove some of the heat in the combustion products and prevent ignition of other things in the vicinity.

Dr. COHEN asked if it was possible to express the flame-quenching ability of the various types of devices discussed in terms of pressure drop. Was it possible to say which was the most efficient in terms of pressure loss, as that was an important factor in design? Taking two very different types of arrester, the packed column and the sintered metal arrester, Dr. Cohen asked if there was any advantage of one over the other in that respect?

Mr. PALMER said that he had not examined the problem but in general there was probably a correlation between pressure drop and quenching ability, as specified by the maximum velocity of flame just quenched by the arrester. The correlation would probably apply to arresters containing smooth-walled passages but might not apply, for instance, to randomly-packed gauzes. For ordinary working, the flow would be streamlined and the pressure drop would vary with the diameter of the aperture, d, and the length of the passage, y, possibly depending on y/d^2. However, it was essential that the diameter of the aperture should not exceed the critical quenching diameter, otherwise the arrester would fail no matter how thick it was. An arrester could be designed to give a certain pressure drop at a certain flow-rate by making it very thick and with passages of large diameter. But such arrester would not quench flames. With a packed-tower arrester the passages through the arrester varied in width and it was essential that none was sufficiently wide to allow flame to pass. Measurements of pressure drop would give only an average value.

A convenient method of causing a substantial reduction in pressure drop was to enlarge the duct where the arrester was installed. The widening of the duct reduced the velocity of the gas passing through the arrester and so reduced pressure loss.

Mr. A. V. BAILEY asked if there was any simple relationship between the flame-quenching performance of arresters and the heat to be removed per unit volume of either the combustible mixture or the products after combustion.

He was thinking particularly of the prediction of the performance of arresters with combustible mixtures containing hydrogen from results obtained with hydrogen alone.

Mr. PALMER said that in burning stoichiometric mixtures of a wide range of hydrocarbons and similar compounds in air the total amount of heat released did not vary much. In fact, it was necessary to extract about one-quarter of the heat released in the flame front in order to quench the flame (including hydrogen flames). It might not be the case for detonations in hydrogen and in other fields.

Mr. H. H. MEYER said that Palmer had stated that the

effect of his type of flame arrester was largely due to heat transfer. A certain amount of heat was generated in the volume taken up by the arrester and passed into the tube. One might expect that as the tube size increased the amount of tube wall per unit volume available for dissipating the heat was considerably reduced. What was the diameter of flame arrester Palmer had used, and what was the limitation in pipe diameter for which these particular devices—wire mesh screen or perforated metals—could be used?

Mr. PALMER said that in the experiments he described the tubing was 2½ in. internal diameter and it was not expanded at the arrester. If the size of tube were increased, and the diameter of the arrester was increased in proportion, the surface area of the walls of passages through the arrester would also increase in the same proportion. There would thus be the same area of passage wall per unit volume of flame. The amount of heat transferred to the arrester in quenching a flash of flame was so small that it raised the temperature of the arrester only a few degrees.

Some further experiments had been done with a duct of one foot diameter and the effectiveness of the perforated plate arresters was not markedly different. The work was still in progress. With the larger diameters, mechanical failure of the arresters became a problem. Wire gauzes and thin perforated metals were flimsy and tended to disrupt or bend. By using external bracing, with more robust arresters, the problem could often be overcome by simple mechanical means.

Mr. E. WOOLLATT asked if he was correct in thinking that, in order to apply the result reported by Palmer, one had to decide with what velocity the flame was likely to arrive at the arrester. That would depend upon the distance from the point of ignition and the various other factors.

Mr. PALMER said that that was so, and it was one of the difficulties. The main intention had been to compare the different types of arrester and determine what type of flame they would withstand. There was also the problem of the type of flames in the practical system. Attention should be paid also to the provision of vents because if venting was provided to keep flame speeds down, the arrester could be relatively coarse. If it did not have to withstand flames having speeds of hundreds of feet per second, the provision of an arrester was much easier. One would look askance at any system where one had 20, 30, or 40 ft of pipe which could contain a flammable fuel/air mixture with no protection in it at all. If such a system were installed a very effective arrester would be required. Those described in his paper would not be sufficient, but they would be practicable, and have quite an economic attraction if vents could be provided to keep flame speeds down so that the arrester itself was never exposed to a very fast flame.

Mr. D. M. ELLIOTT said that he was using combined explosion boxes and flame arresters filled with 1 in. Raschig rings. From Palmer's results it appeared that no exact criteria could be applied to the design of such arresters, since the random nature of the packing made it a matter of pure chance whether sufficient passages would be obtained of the very small diameter required to quench the flame. In the paper by Rasbash and Rogowski it had been noted that obstructions to flow tended to increase the explosion effect downstream of the obstruction, and in that way a random packed bed might perhaps have the opposite effect to that desired.

Could Palmer comment on the effectiveness of that type of arrester, and in particular had he any experience with these or the perforated plate type handling gases liable to detonate such as hydrogen or acetylene?

Mr. PALMER said he had not worked on acetylene.

Raschig rings would be effective provided that they were sufficiently small and there were enough of them to prevent excessively wide continuous channels through the bed. For instance, with propane/air mixtures, a channel ⅛ in. wide or more would permit a flame to propagate slowly through the layer. However, the whole subject needed detailed investigation. Problems of how thick to make the layer of rings, the size of the rings and their arrangement, and the types of explosion that would be arrested all required systematic study.

The increased explosion effect downstream of an obstruction, as noted by Rasbash and Rogowski, would occur if turbulence were generated. But with packed towers the flow through the bed would often be streamlined, so that a serious increase in explosion violence would not be expected.

Dr. J. H. BURGOYNE said that, in his view, an important point had been brought out when attention was drawn to the fact that the performance of the flame arrester depended on the rate of flame propagation but that there would be lack of knowledge of that in a particular case. There was a possible answer which was that there was a limiting value to the rate of flame propagation after travel over long distances which might in some cases be the detonation velocity, or might, in others, fall short of that value. It was possible, as Simmonds and Cubbage had shown, to cope with the limiting speeds of explosion with arresters of the crimped ribbon type.

Dr. SIMMONDS said that the object of the work was limited to flame traps for use with town gas/air mixtures. That was to say, a situation where one deliberately made a pre-mix. They assumed that if they could show that an arrester or flame trap existed which was not intolerable on grounds of pressure drop or anything else, and would stop detonation, that it was the answer to all the problems because one could obviously use it and the pressure drop would not be prohibitive.

They had been able to get a solution to that situation, using a crimped ribbon arrester in a special form of housing. The object of it was that there was a deceleration of a flame when it reached a sudden enlargement. Using that system, they had data which enabled flame traps to be designed for pipelines up to 4 in. diameter and, by extrapolation, up to 8 in. Crimped ribbon arresters were, of course, commercially available. The housings were not yet available but were not difficult to make.

They had had their special field of gas/air premix to consider, but since they were considering detonation, and since gas/air detonation velocities were very similar, the system could obviously be applied to other fuel/air mixtures. The arresters and traps did stop detonation; the dynamic pressure on the trap was of the order of 20 atm when detonations reached it and it did withstand them. That meant that they could be used under quite high pressure situations on an outlet to a tank.

With regard to plastic arresters: in the course of the work they had used arresters (they might be called crimped ribbon arresters) made of gummed brown paper about 1 in. wide as used for wrapping parcels. If that paper was moistened and fed into a crimping machine an arrester could be fabricated

which would stop detonations as well. It only lasted for two or three detonations because the leading edges of the paper became distorted. There was no great practical significance in it except it did emphasise the point that the material actually used had no great significance.

Dr. L. L. KATAN referred to Palmer's statement that only one-quarter of the heat of the flame had to be removed. Did that not suggest that the mechanism was not quite so simple as mere heat removal, and that possibly the true mechanism in many cases was the interruption of free radical and, perhaps, energy chains?

Mr. PALMER said that that was a question that frequently occurred throughout the field of flame propagation: to what extent propagation was the result of conduction of heat into unburnt gas and to what extent it was the result of diffusion of active particles ahead of the flame front. Both processes obeyed the same mathematical laws, so they could not be separated by writing down a few equations to see which described the effects. One point which put him in favour of a heat transfer mechanism for flame arresters was that the nature of the surface to which the flame was exposed when it was quenched did not matter. In particular, metals coated with substances like potassium chloride, which were known from work on reaction kinetics to be effective chain breakers, did not acquire enhanced flame arresting properties. Determinations have been reported of the quenching diameters of different gas mixtures in tubes coated with various materials, including reaction chain breakers, but no effect was detected. The suggestion was then made that all surfaces were 100% effective in terminating chain reactions. The fact that that suggestion was necessary tended to count against the theory, but did not disprove it.

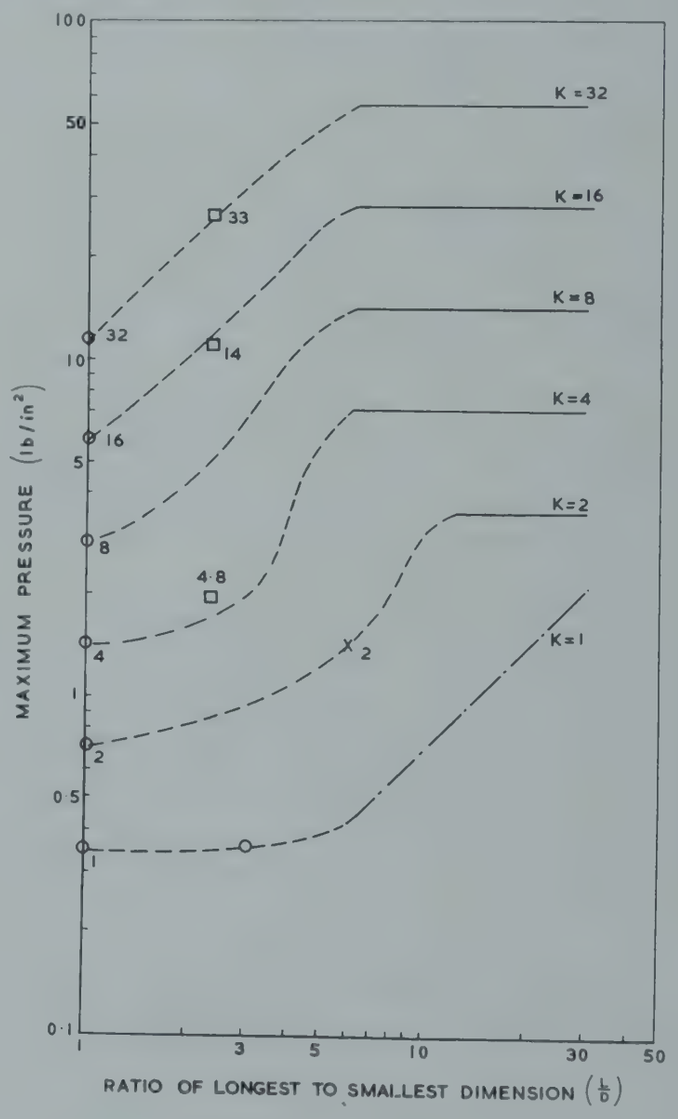
Mr. D. BRADLEY said he believed that in the absence of over-riding considerations it was common practice to site flame arresters in the coldest part of the system. Could Palmer comment on that in view of the fact that heat transfer was not a controlling factor?

Mr. PALMER replied that, so far as he knew, there was no general recommendation that the flame arrester should always be put in the coolest part of the system. The temperature difference between the flame and the surface was about 1800°C. If the flame arrester was at 100°C instead of, say, 20°C the temperature difference between it and the flame had only changed by 5%. However, the rate of burning of gas mixtures varied with the initial gas temperature more markedly, and so a flame would propagate more rapidly through hot combustible mixtures than through cold mixtures. As the flame speed at the arrester should be as low as possible, there was something in favour of installing the arrester in cool gas, provided that blockage due to condensation of volatiles would not be a nuisance.

Dr. SIMMONDS said that a flame trap should be sited as near as possible to the probable point of ignition.

Dr. M. J. G. WILSON said he had tried to compare the results of the three papers on explosion relief in terms of the relation between the maximum explosion pressure expressed in pounds per square inch gauge and the ratio of the vessel cross-sectional area to the vent area, K. Simmonds and Cubbage, with coal gas in roughly cubical enclosures, found that P was about equal to K. Rasbash and Rogowski, with propane or pentane in long narrow ducts, found $P = 0{\cdot}8$ to $1{\cdot}8\ K$. Burgoyne and Wilson, in the second session, with pentane in short cylinders, reported $P = 1$ to $1{\cdot}5\ K$ for undisturbed explosions and $P = 3$ to $4{\cdot}5\ K$ for violent explosions with rich mixtures.

Dr. RASBASH said that they had attempted a correlation of the type described and broadly they had found that they could correlate results fairly well, except for the results of Burgoyne and Wilson for small vents (*i.e.* vents with a large K factor) in a large vessel of $L/D = 1$, approximately. The correlation obtained is shown in Fig. 1 in which the maximum pressure was plotted against the ratio of the maximum to the minimum dimension of the vessel for different K factors.



PROPANE—AIR MIXTURE

O = Based on the work of Simmonds and Cubbage

X = Point obtained at J.F.R.O. for $K = 2$ with a 6 ft duct of 1 ft square section

□ = Cousins and Cotton. Volume of vessel = 3.0 ft²

——— = Equation (2) of paper by Rasbash and Rogowski

— · — = Equation (3) of paper by Rasbash and Rogowski

The numbers refer to the values of K

Fig. 1.—*Relation between maximum pressure and length to diameter ratio for different vent ratios*

The correlation was based on the work of Simmonds, Cousins, and Cotton and the authors. It would be noted that there was a general tendency for the maximum pressure to increase for a given value of K between 2 and 32. The reason for the increase in pressure was that turbulent flow was becoming established along the duct which increased the rate of combustion and the flame speed; the reason for the constant pressure was that the flow had become established and the flame speed was approximately constant. However, even for values of K between 2 and 32, it had been found at Fire Research Station that the maximum pressure rises again for values of L/D in excess of 30. The reason for that increase was not clear, but it had been observed that explosions taking place under those conditions were accompanied by intense vibrations which might have brought about a further increase in the rate of combustion. Results of Burgoyne and Wilson showed maximum pressures which were higher than given by the correlation, although there was some evidence that they tended to extrapolate towards the correlation for low values of K. As indicated by those authors, the reason for that difference might be the distortion of the flame caused by disturbances in the unburned gas flowing through the vent. On the other hand, the results of Swedish work[1] indicated that correlation might be applied with only a small error for a large vent in a vessel of very large volume (7000 ft^3) with values of L/D and K approximately unity.

Mr. E. C. B. Bott said that it was difficult to find out if one had allowed for all possible hazards, particularly with new organic chemicals. Was there any printed procedure that would tell people how to go about the job in a better way than just working off their own bat? Often, ducts contained small amounts of solids, such as dust, in suspension. Polythene ducts and mild steel ducts had been mentioned. Some organic substances produced electrostatic properties. Could Rasbash say something about the differences between these organic polymers and steel regarding their electrostatic properties?

Dr. Rasbash said that the Joint Fire Research Organization was always very pleased to answer people's queries specifically. Queries from industry were welcomed. The Factory Inspectorate was also very active in this field.

The Joint Fire Research Organisation had not done any work on the development of static charges in dust. A considerable amount of work had been done in Germany on the development of static charges in dusts flowing through ducts. If the nature of the dust and the tube were approximately the same, there was not as much charge formed as if they were quite different. Work had been done at the Bundesanstalt für Materialprofung in Berlin.

The use of polythene was suggested as a way it might be done; there were other ways of building a duct so that it would disintegrate safely, or explode safely when a flame passed through it, and which would prevent the flame increasing in speed. Polythene might not be good for duct carrying because the dust might abrade the polythene in a short time. A very light duct which was hard and which would fly open in a controlled manner might be a possible answer.

Reference

[1] *Report of Kommitten für Explosions Forsok*, 1957. (Stockholm: Kommitten für Explosions Forsok.)

PAPERS AND DISCUSSION AT THE FOURTH SESSION

HAZARDS IN HANDLING ACETYLENE IN CHEMICAL PROCESSES PARTICULARLY UNDER PRESSURE

By S. A. MILLER, B.Sc., M.A., Ph.D., F.R.I.C.* and E. PENNY, B.Sc., A.R.C.S.*

SUMMARY

The explosive limits of acetylene in air are particularly wide—from 2·5 to 80%. All possible sources of ignition in the plant area must be eliminated, to avoid the risk of igniting flammable mixtures resulting from leaks in plant items. This includes the enclosure of any electrical equipment in the neighbourhood of the acetylene or to which leakage could penetrate, the housing being pressurised with air to a few inches water gauge. Decomposition of acetylene (on its own) liberates 54·1 kcal of heat per mole, and compressed acetylene can behave as a high explosive. Nevertheless commercial plants have been operated at pressures up to 20 atm. Possible sources of ignition within the acetylene-containing system must be avoided: these include silver and copper (or alloys of more than 70% copper), as decomposition of their acetylides can initiate explosions of the compressed acetylene.

Reactors should be heated by hot fluid rather than by electricity, and never by flame. Plant items need to be constructed so that if acetylene decomposition does occur within them detonation could not occur but the reaction should remain deflagration. Vessels should be designed for a test pressure of about 11 times the operating pressure, so that they will not burst when subjected to deflagration. Detonation can build up in long lengths of pipe lines and the pressure can rise by factors of 40-45 in the front of the explosion wave. Long lengths can be buried or laid in deep trenches and explosion arrestors be inserted where appropriate to prevent detonation passing into more sensitive items of equipment. With wide pipes, at pressures up to 30 lb/in²g, a tower filled with Raschig rings can be used to quench detonation. Reactions have been carried out experimentally without disaster at up to 150 atm when the reacting system was entirely a liquid phase, with no accompanying vapour, without using the 11-fold test-pressure factor.

Introduction

Acetylene has been available commercially for some sixty years, but for the first thirty years its main uses were for illumination and for the welding and cutting of metals ; the only large-scale use in chemical synthesis before 1925 was the preparation of acetaldehyde which was developed during the first world war. The use of acetylene as a fuel gas is still increasing, but now there is a much greater and more rapidly rising demand for acetylene for a variety of large scale chemical syntheses which have been developed in the last two or three decades.

Most of the acetylene used in these processes is at about atmospheric pressure or only up to about 1 atm g. In addition to the manufacture of acetaldehyde already mentioned, the syntheses for which acetylene is required include vinyl chloride, vinyl acetate, other vinyl esters, acrylonitrile, acetylene black, trichloroethylene, vinylacetylene (for neoprene), etc. There are hazards when working with acetylene even at pressures such as 1 atm g, but much more serious additional hazards arise when working with acetylene at higher pressures. In Germany during the early part of the war large-scale processes were operated requiring the use of acetylene under pressure and the explosion hazards were kept under control. The largest of these processes was the production of butynediol, and a plant of capacity 30 000 tons per annum was operated at Ludwigshafen by I.G. Farben. The product was used as an intermediate in the manufacture of Buna rubber. Other processes using acetylene under pressure include the manufacture of polyvinylpyrrolidone, of some vinyl ethers, and of acrylic esters. Some of this work was taken up in America after the war, and to a smaller extent in other parts of the world.

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Nature of the Hazards

Flammation

The main hazard in dealing with acetylene at normal pressure—a hazard which, of course, is present with compressed acetylene—is that which is common to all flammable gases. This is the danger of explosive flammation, either within the plant through adventitious ingress of air, or externally, following leakage of the flammable gas. This danger is, however, particularly acute with acetylene, because it has such wide explosive limits when mixed with air, *viz.* 2·5–80%. Explosion could follow leakage into a fairly confined space, being initiated by a flame or by a spark from electrical equipment ; as yet no electric motors or switchgear have been certified as " flameproof " for use in acetylene-containing atmospheres.

Initiation of explosive acetylene decomposition

The other hazards with compressed acetylene arise from its ability to decompose exothermally under certain conditions in complete absence of oxidising or other reactants. It is thermodynamically unstable in respect of its elements at room temperature, and the overall reaction $C_2H_2 = 2C+H_2$ liberates 54·1 k cal per mole.

All the recorded ways of initiating the explosion of acetylene under pressure involve the production of a point of local heating. The decomposition temperature of acetylene at 2 atm abs has been stated to be 510°C.[1] The present authors

have measured the temperature at which acetylene at 3–25 atm g becomes subject to explosive decomposition, by admitting acetylene into a heated steel tube which had previously been evacuated. The explosion temperature is independent of pressure over the range studied, but it is reduced considerably by the presence of small amounts of finely powdered materials. The results in Table I were obtained with 1 gram of such powders at the centre of a pipe 15 in. long and ½ in. diameter ; and the powdered materials examined included rust, pipe-scale, kieselguhr, alumina, silica gel, and charcoal.

TABLE I.—*Temperature needed to Initiate Explosion of Acetylene in Steel Pipe at 3–25 atm*

Clean empty tube	400–425° C
In presence of 1g of powder	280–300° C
In presence of 1g of solid potassium hydroxide ..	170° C

The authors believe that exothermic condensation reactions occur on the surface of the solid material which raise its temperature to the 450°C needed to initiate gas phase decomposition.

It is well known that certain acetylides, particularly copper and silver, are themselves capable of explosive decomposition. The explosion of copper acetylide is rarely in itself a hazard because the quantities of this material normally isolated and handled or obtained adventitiously in the use of acetylene are small. The intrinsic hazard of copper acetylide is the capacity of certain varieties to decompose upon extremely mild initiation, and thereby produce hot spots sufficient to set off acetylene decomposition.

This was illustrated by preparing a particularly sensitive variety of copper acetylide, as a black flaky material, by bubbling acetylene through slightly acidic solutions of cupric salts,[2] and drying the precipitate. A fragment was placed on an anvil inside a tube, to which acetylene was later admitted at a pressure of 3 atm.

A ¼ in. steel ball was magnetically held 15 in. above the anvil within the tube, and then allowed to drop. This was sufficient to decompose the copper acetylide, which in turn set up an explosive decomposition in the gaseous acetylene. The apparatus is indicated in Fig. 1.

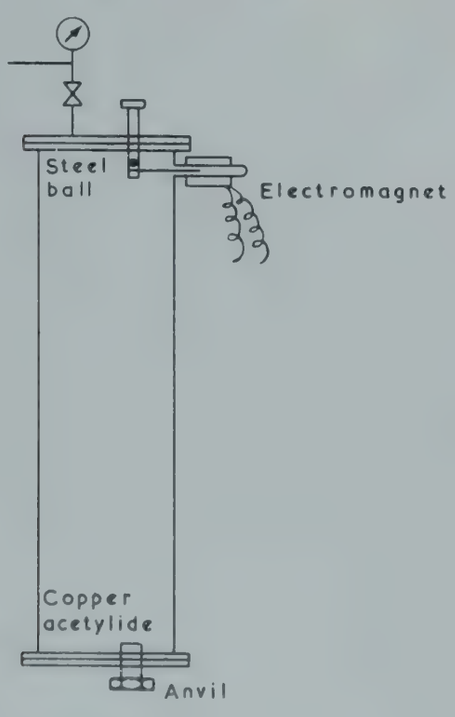

Fig. 1.—*Ignition of acetylene by impact of copper acetylide*

Copper acetylide can also be formed from metallic copper by prolonged exposure to acetylene, particularly if the surface of the copper has previously been corroded. The nature of the film is dependent on the copper content of the alloy. If this is low (less than 65–70%) the acetylide film (if formed at all) remains extremely thin and adherent to the metal ; such films cannot be made to spark by friction or by contact with a wire heated to 150°C. Copper acetylide films on alloys of higher copper contents or on pure copper can become thicker, and it may be possible to flake them off the surface of the metal. If detached from the metal, this acetylide is still not as sensitive as that formed by wet methods from copper salts, and cannot be ignited by the steel-ball test described, but it is still sufficiently sensitive to be ignited by friction or by hot wire at 150°C.

Explosive complex mercury acetylides can be formed by passing acetylene through solutions of mercuric salts under particular conditions. Mercury acetylides cannot however be formed directly from metallic mercury and acetylene, even in presence of dilute acids.

Silver acetylide is readily formed when acetylene is passed through silver nitrate solution. It is intrinsically a much more powerful explosive than even the most sensitive copper acetylide. Equal amounts of silver and copper acetylides were placed in test tubes behind Perspex screens ; the acetylides were then exploded by electrically fusing a wire embedded in them. The copper acetylide decomposition was contained within the glass test tube, but the exploding silver acetylide shattered the tube and also fragmented the Perspex screen. Detailed study of the type of acetylide formed directly from silver and acetylene is not available, but the authors have observed explosive deposits on silver solder exposed to acetylene.

Nickel does not form an acetylide.

A possible source of point-heating in acetylene could be the frictional hot spots produced on opening a valve, especially if a fragment of grit has become lodged in the seating. In the ordinary use of acetylene in industry, valves are opened millions of times annually to allow passage of compressed acetylene from cylinders, manifolds, compressors, etc. Perhaps one in a hundred million of such valve openings has been followed by a sequence of events finally resulting in an explosive acetylene decomposition, but there have been so few that it has not been possible to discover whether the primary initiation of the explosion was friction within the valve or some highly adventitious accompanying cause. In the authors' own experimental work, initiation of this type was experienced only once, and this was when using a cock in which a stainless steel spindle rotated within a non-metallic sleeve (and frictional hotspots would be therefore least expected). Acetylene was being passed at a pressure of 18 atm into a closed pipe, 2½ ft × ¾ in. containing air at atmospheric pressure. There was a piece of platinum wire, 1 cm long, at the far end of the pipe. The explosion started when the cock was one-third open, but the mechanism of initiation could not be elucidated.

In spite of the field experience, it was suggested some years ago[3] that valves with metal-to-metal seatings were capable of initiating acetylene explosions. The authors attempted to investigate this experimentally. A test valve was placed between two vessels, each 3 ft × 3 in., and the valve was opened and shut mechanically. The apparatus is shown in Fig. 2.

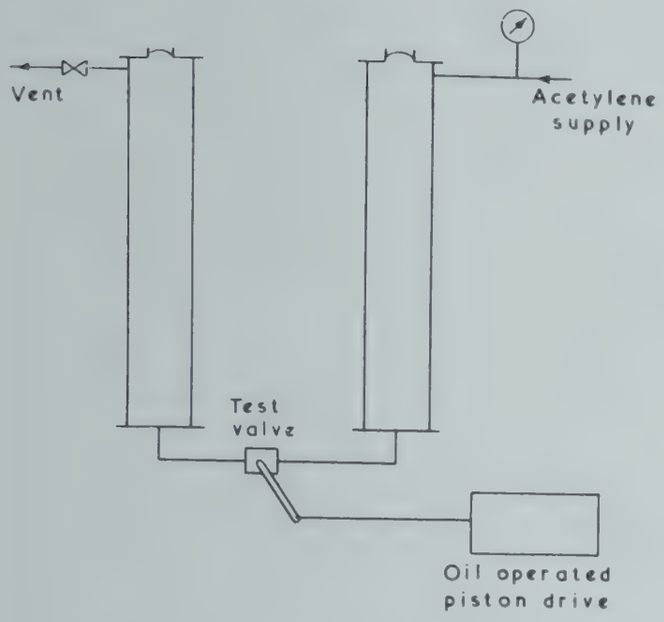

Fig. 2.—*Automatic valve-tester*

The first vessel was connected to an acetylene compressor so as to maintain its pressure at 20 atm. The second vessel had another valve which was kept slightly open, so that acetylene flowed through the whole system each time the test valve was opened. The test valve was opened and shut 10 000 times, and no decomposition was initiated in the acetylene.

In order to see whether this negative result applied only to a clean valve, a little concrete dust and iron rust was put into the seating of the valve, and the experiment was repeated for another 10 000 operations. No explosion was initiated. In a further experiment, the foreign material introduced into the valve seating was a mixture of charcoal and copper acetylide, and here again no explosion could be initiated by 10 000 operations of the valve.

Deflagration

The 54·1 k cal of heat liberated in the decomposition of a mole of acetylene would be sufficient to raise the temperature of the resulting carbon and hydrogen to 3100°C if there were no heat loss. At this temperature, however, there would be an equilibrium concentration of about 6% of acetylene. The authors have analysed the residual gas after the experimental explosive decomposition of acetylene (initially at 3·4 atm abs) in a long pipe, and found that it contained no acetylene, but consisted of 92·2% hydrogen, 5·5% methane, and 2·3% olefines (mainly, and possibly entirely, ethylene). It is thought that there may nevertheless have been acetylene in the explosion wave front, and that the methane and ethylene were formed from it, in presence of the hydrogen, during the cooling down after the explosion wave had passed. If allowance is made for the undecomposed acetylene in equilibrium at the high temperature, and also for heat absorbed in some dissociation of hydrogen molecules into atoms, it can be shown that the temperature reached on decomposition (assuming no heat loss by radiation, etc.) would be between 2800 and 2900°C, depending somewhat on the initial pressure of the acetylene (since the dissociation equilibrium of hydrogen molecules is pressure dependent). This temperature would give a rise in pressure by a factor of $10\frac{1}{2}$–11.

Rimarski[4] records the explosion of acetylene initially at 1·40 atm abs in a vessel of 27 cm diameter ; his final pressure was 13 atm abs, a rise by a factor of 9·3. The authors have carried out several determinations of pressure rise in a vessel 12 in. × 2 in., initiating acetylene decomposition by the fusion of a platinum wire 1 cm long × 0·2 mm. In 16 experiments with an initial pressure of 9·0 atm abs the average final pressure was 100·2 atm abs (with a standard deviation of only 5·3 atm). This pressure rise of 11·1 times agrees very well with the calculated factor given above.

The time taken for the pressure rise to occur was also measured ; the time between initiation and the onset of pressure rise was variable, being anything from 3 to 45 ms, but the pressure rise itself always occurred in 3 ms or less, as shown by Fig. 3.

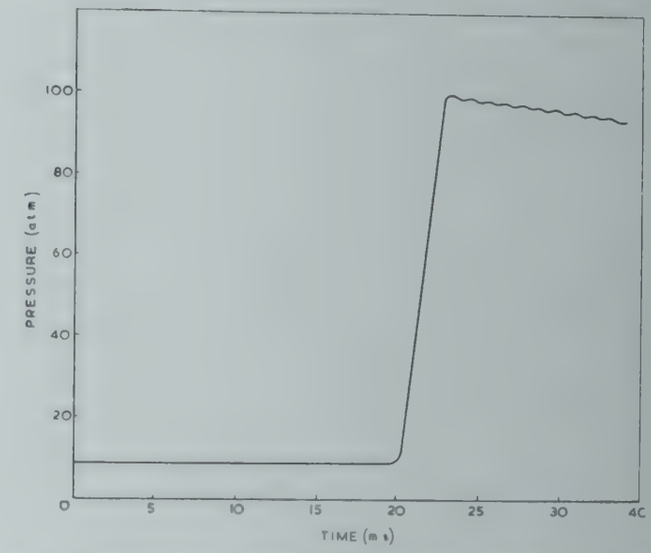

Fig. 3.—*Pressure-time record for deflagrative explosion of acetylene*

The experiments had been designed to determine the velocity of deflagration, but, as stated, the time measured over the (fixed) distance between the fused wire and the pressure gauge was unreproducible, and the velocities measured ranged from 10–100 m/s.

It had long been believed that there was a minimum pressure of 1·4 atm abs (5·9 lb/in²) below which self-propagating explosions could not be induced in acetylene.

The critical minimum pressure had been related to the diameter of the pipe, decreasing with increase in diameter to the above value for the widest pipes[5] as indicated by Fig. 4.

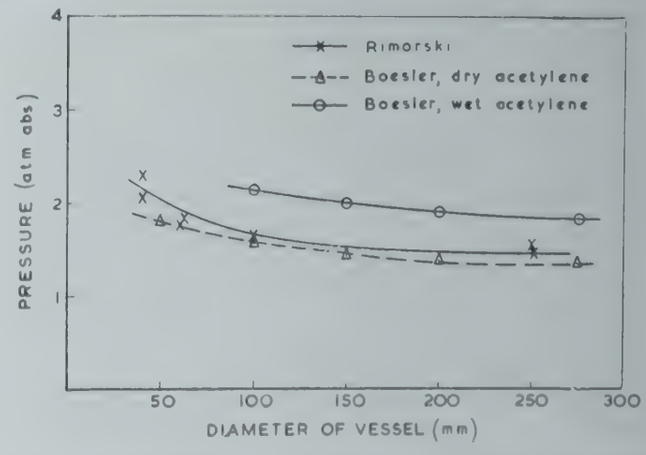

Fig. 4.—*Limiting pressure for decomposition of wet and dry acetylene as a function of vessel diameter*

It was therefore considered that acetylene could safely be piped over indefinite distances if the pressure was not much above ambient, say that of a gasholder (12 in. water gauge 1·03 atm abs). On 2 January, 1954, however, a serious explosion occurred at Chemische Werke Hüls, involving over a mile of pipeline of 6 in. and 12 in. diameter, and attached equipment. In a subsequent study,[6] it was confirmed that progressive decomposition of acetylene could be set up in 12 in. diameter pipe at gasholder pressure, and even at slightly sub-atmospheric pressures, if the initiation occurred across the whole cross-section of the pipe at the same time. This was achieved by using a forechamber with acetylene at a higher pressure (2·5 atm abs), causing the acetylene in the forechamber to decompose by the fusion of a wire, and communicating the explosion to the gas at lower pressure by the bursting of a bursting disc which separated the forechamber from the main experimental pipe. Direct initiation of the lower-pressure gas by the fusion of a platinum wire would not set up a progressive decomposition. Analysis of the conditions of the incident of 1954 suggested that initiation across the whole pipe had indeed occurred by a sequence of mishaps which resulted in the admission of compressed chlorine into the acetylene line.

Detonation

As it travels over increasing distances, the deflagrative decomposition wave accelerates to velocities of some hundreds of metres per second, and the explosion then rapidly passes into detonation, whereby the velocity of propagation rises severalfold ; the pressure developed rises to 20–25 times the initial pressure for a period of many milliseconds (the " Chapman-Jouget plane "), and indeed to 40–45 times for a few microseconds (the " van Neumann peak "). Relationships between onset of detonation and length of pipe, diameter and initial pressure of gas have not been worked out in detail for acetylene, neither alone nor in presence of diluents.

The pressure ratios quoted above have been calculated[7] from classical detonation theory,[8] but the present authors' attempts to measure the pressure rise directly gave inconsistent results. The same calculations[7] led to a velocity of detonation of 2053 m/s for acetylene at an initial pressure of 8 atm abs.

The velocity was then measured in pipes of 1 in. and ½ in. diameter using the circuit shown in Fig. 5. Fig. 6 shows a typical trace obtained on the double beam oscilloscope. In the 1 in. pipe the velocity was 1870 m/s (with standard deviation 22), and in the ½ in. pipe the velocity was 1817 m/s (standard deviation 7). When these results are plotted against the reciprocal of the diameter of the pipe, as in Fig. 7, extrapolation gives a value of 1923 m/s for the limiting detonation velocity in pipe of infinite diameter. The agreement with theory is close enough to show that acetylene behaves like a conventional high explosive, and therefore that the detonation pressures calculated from theory are also of the right order. The discrepancy in velocity between experiment and calculation must arise from incomplete knowledge of the true composition of the detonation wave front; the heat release is slightly less in fact than the amount used in the calculation, possibly because the carbon retains " surface energy ",[9] or contains a slight amount of combined hydrogen, or possibly because some of the carbon is gaseous, *i.e.* its vapour pressure is above that of the equilibrium vapour pressure of solid carbon at the explosion temperature. Enhancement of vapour pressure in gases at high pressure has been observed in several systems.

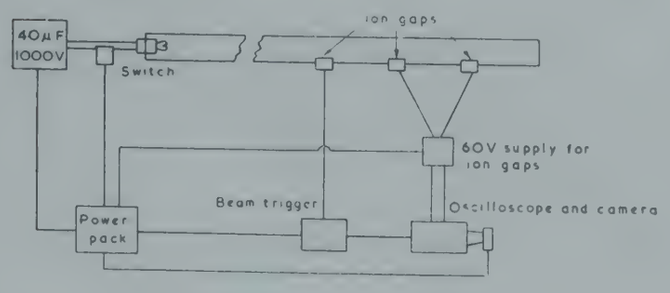

Fig. 5.—*Explosion velocity measurement*

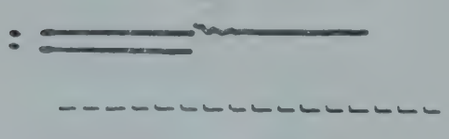

Fig. 6.—*An oscilloscope record*

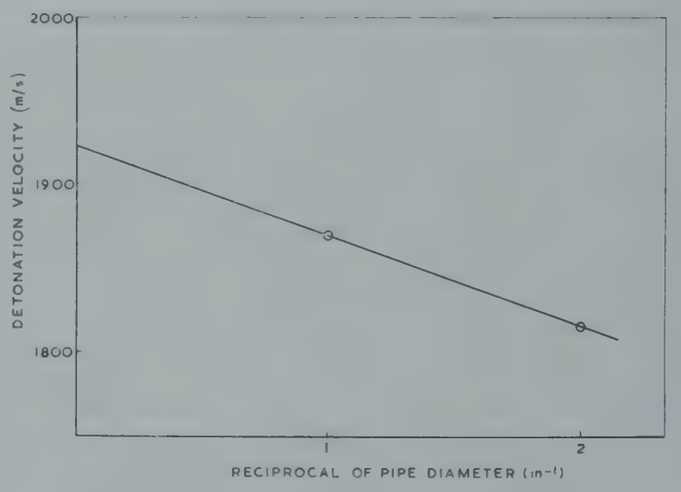

Fig. 7.—*Detonation velocity of acetylene in ½ in. and 1 in. pipes at pressure of 8 atm abs*

Measures Against the Hazards

External flammation

Hazards arising from the ready flammability of acetylene in air demand, in the first place, a high standard of plant construction and maintenance to obviate the possibilities of flammable mixtures being obtained either by ingress of air into plant items or by leakage of acetylene. The plant area should be adequately ventilated, so that even if leakage does occur, the flammable range should not be reached. Even if flammable mixtures should nevertheless transpire in the plant area, the possibility of their being subjected to sources of ignition should be removed. Obviously naked flames must be excluded, but in addition electric starters, switchgear, and motors should be housed in separate rooms or enclosures away from the plant.

In the authors' work on the use of acetylene for chemical processing, all the electrical equipment, including lights and wiring, was enclosed and the enclosures and conduit were pressurised with dry air to a pressure of a few inches water gauge. This ensures that any leakage of flammable material would not come into contact with potential sources of electrical ignition.

Sources of internal initiation

Since acetylene can be initiated by a surface at 425°C or by powdered material at 280°C, vessels should not be heated by direct flame, and preferably by hot fluids rather than directly by electricity.

Copper and high-copper alloys need to be avoided for vessels and pipes containing pressurised acetylene ; even low-copper alloys are best avoided for substantial items of plant, especially where there is any possibility of corrosion by acidic agents. Brass or bronze fittings external to the plant do not present much hazard. They can (and should) be kept clean by good housekeeping, and appreciable deposits of acetylide should not be allowed to build up. Even if they did, the copper acetylide deposit on the brass or bronze is not sensitive, and is not in places where it could set off an explosion in pressurised acetylene. Even small amounts of silver in any form need to be excluded from plant using compressed acetylene.

The use of mercury in instruments attached to acetylene-using plant does not in itself appear to produce a source of hazard. Nickel and nickel alloys can be used freely where needed. There seems to be no case for preferring any particular type of valve from safety considerations alone.

Vessels

In spite of all precautions to avoid sources of initiation, it has to be accepted that initiation of explosion may nevertheless occur, and reactors, etc., need to be strong enough not to burst even when such an explosion occurs. In order not to impose an unnecessarily heavy design factor the vessels need only be such as to withstand deflagration but not detonation pressures : measures to ensure that detonation cannot take place within them will be discussed later.

The pressure-rise in deflagration is about 11-fold, so that vessels built to a test pressure (not a working pressure) of 11 times the working pressure are needed.

Some work has been carried out to see whether this safety margin could be reduced by incorporating appropriate bursting discs in a vessel. A test vessel 15 in. × 4½ in. was fitted at one end with a bursting disc of 2 in. diameter set to operate at 32–33 atm. Explosions in the acetylene in the vessel were initiated by the fusion of platinum wires at various distances from the bursting disc, and also by passage of an explosion into the vessel through a ½ in. diameter pipe attached to the midpoint of the vessel wall. The explosion pressures were measured by condenser gauges at various points within the vessel.

TABLE II.—*Some Explosion Pressures in a Vessel with a Bursting Disc to fail at 32 atm*

	(atm)	(atm)
Initial acetylene pressure	10	20
Pressure near bursting disc :		
Explosion initiated at furthest point	50	136
Explosion led in by attached pipe	70	150

Thus even a bursting disc relatively large compared with the diameter of the vessel cannot prevent pressures much larger than the operating pressure of the disc being experienced, although it does somewhat reduce the full 11-fold rise in pressure which would otherwise be attained. The protective value of bursting discs for this purpose is therefore limited.

Bursting discs may however be valuable in reactors with gas and liquid phases, as reactions between acetylene and other reactants in the liquid phase may accelerate without becoming explosive ; a bursting disc would effectively limit the rise in pressure consequent on acetylene (and other solutes) being forced out of solution by the heat liberated, and therefore may prevent a gas-phase explosion which might otherwise ultimately occur.

Reaction vessels need to be of such dimensions that deflagrations initiated within them cannot pass into detonations. This is a function of the length to diameter ratio of the maximum gas space which might be present in various stages of use, and of the working pressure. Work in pipes of ½ in.–12 in. diameter suggests that the length to diameter ratio for detonation to build up drops from about 200 : 1 at 15 lb/in²g to 10 : 1 at over 200 lb/in²g.[10] No measurements are available at 300 lb/in²g. It seems that an adequate margin of safety would be maintained if acetylene gas phases under high pressure in reactors were limited to regions of not more than 3 ft long and 1 ft diameter. If the scale of operation demanded larger gas spaces than this, considerable further study of the build-up of detonation would be needed.

Considerable importance has been attached in reports of the German plants using acetylene at pressures higher than 5·5 atm abs to the use of diluents, particularly nitrogen. For example, in the German vinyl ether process[11] operating at 18–22 atm the proportion of nitrogen in the recycle gas was 55%, and after injection of fresh acetylene, the gas fed into the reaction vessel contained 45% nitrogen. Experimental work in Germany[5, 12] had however previously shown that the proportion of nitrogen needed to make a mixture non-explosive at 20 atm was 65% at 15°C and 70% at 100°C. The results of tests in a tube 1m long × 9 cm with acetylene-nitrogen mixtures at up to 200 atm are shown in Fig. 8. The present authors, working with a 1 in. pipe, found that a mixture containing 48% of nitrogen would sustain progressive explosion even at a total pressure of only 7 atm.

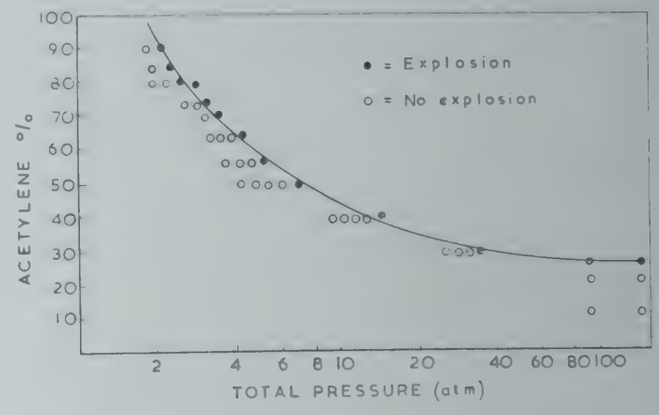

Fig. 8.—*Limiting pressure for explosive decomposition of acetylene nitrogen mixtures*

In general, the extent of dilution needed to suppress completely the hazard of explosive decomposition of acetylene is such that it would be intolerable in manufacturing processes, as it would effectively reduce the partial pressure of acetylene for reaction purposes. There may be a region of dilution in which explosions are more easily confined to deflagration rather than detonation, but these regions have not been delimited. The authors' evidence, as far as it goes, suggests that detonation still remains possible if the length to diameter ratio is high enough, even at appreciable dilution. The hazards which have to be faced and allowed for are not appreciably reduced by the introduction of diluents in reasonable amounts.

Explosion arrestors

It has been seen that it is advisable to build reactors and other vessels to withstand deflagration explosion without bursting, and to limit their size so that detonation cannot develop within them. It is essential to ensure that detonation cannot be passed into such vessels from pipe lines attached to them.

The problem of superimposed detonation can arise either from wide pipes carrying acetylene at comparatively low pressures over long distances, or from narrower pipes carrying the compressed acetylene from stage to stage within the high pressure plant.

As has been shown, pipes of 12 in. diameter can sustain acetylene explosion even at atmospheric pressure. Even if the acetylene is to be used at or about this pressure, it is often desirable from considerations of the operation of the plant to convey it at pressures of perhaps 15 or 22 lb/in^{2}g (which are commonly used for this purpose). At such pressures, pipelines of less than 12 in. diameter also introduce the possibility of adventitious explosion of acetylene in the pipeline, and if the line is long enough, such decomposition may progress into detonation. If Class C seamless pipes are used, the pipe itself is usually strong enough not to rupture even when detonation occurs, but in some installations it has been deemed advisable to bury as much of the pipe as possible, or to introduce some other means of protecting personnel. Equipment at each end of the plant might however include items built to withstand deflagration but not detonation, such as compressors or reactors, or items which cannot be reasonably built to withstand even deflagration and in which deflagration is extremely unlikely to be initiated in the items themselves, such as gasholders, gas meters or purification systems. To counter the hazard of communicated explosion, installations have been designed for use at the end of long pipelines to quench an explosion wave, whether it is deflagrative or detonative in character.

One such type of explosion arrestor was tested by Schmidt and Haberl[6] and is in use in America and Britain. Essentially it comprises a tower packed with Raschig rings which are irrigated with water. The authors have tested such a tower, 10 in. diameter packed with 1 in. Raschig rings to a depth of 4 ft and attached to 600 ft of 3 in. diameter line containing acetylene at 30 lb/in^{2}g (3 atm abs). The apparatus is shown in Fig. 9.

Initiation of the explosion was effected across the whole diameter of the pipe by attaching to the end of the pipe furthest from the tower a 3 ft length of pipe separated from the main run of pipe by a bursting disc. The pipe contained acetylene at 8 atm abs. The acetylene in the forechamber was exploded by the fusion of a platinum wire 1 cm $\times$ 0·2 mm, using a 24v battery. The velocity of the explosion wave before it entered the tower was 1750 m/s, which confirmed that detonation was set up.

Pressure measurements were attempted, using condenser gauges at various points in the tower, but the records were confused by oscillations caused by vibrations induced in the steel of the tower walls. Thermocouples showed that there was no rise in temperature 1 ft above the point of entry of the explosion into the tower. Indeed, the evidence from visual examination showed that the explosion had been completely quenched in the first few inches of the tower. The system as tested was, however, completely closed, and even though the explosion was quenched, bursting discs set to operate at 10 atm functioned either at the top of the tower or at the end of the 20 ft run of outlet pipe from the tower. A considerable amount of gas in the pipe had been heated to some 2800°C and raised to a pressure of about 70 atm ; this gas did not instantaneously revert to atmospheric temperature and pressure after the passage of the explosion wave so that a pressure-pulse in excess of 10 atm passed into the gas beyond the tower, into gas in which no explosion had occurred.

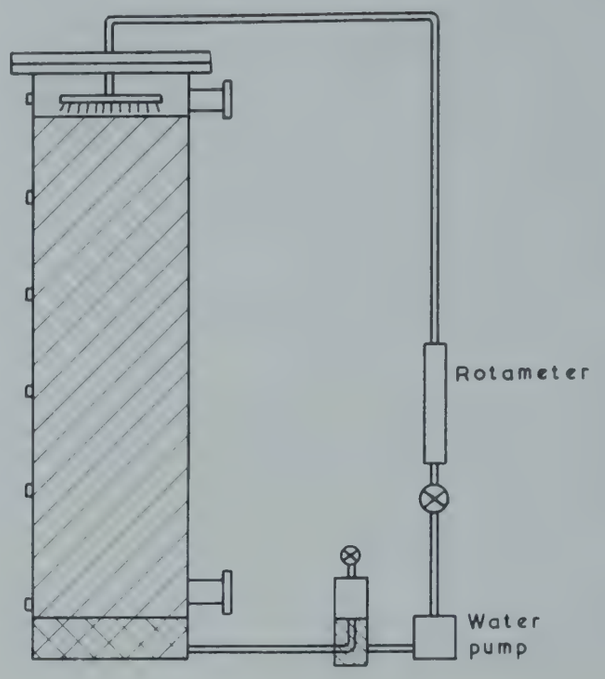

Fig. 9.—*Water-irrigated packed-tower explosion arrestor*

This pulse would be undesirable in practice, so a bursting disc functioning at 10 atm was inserted on a T-junction near the point of entry to the tower. The outlet from this disc was arranged vertically upwards. When the acetylene in the pipeline was exploded, the functioning of this disc provided an escape for gas and the pressure-pulse passing through the tower after the quenching of the explosion was limited to about 50 lb/in^{2}g, *i.e.* less than twice the original pressure.

Further work showed that complete quenching of the explosion (and limitation of the pressure-pulse) could be achieved even with dry Raschig rings in the tower, except that under such conditions the explosion was only completely quenched after it had traversed 1–1½ ft of the rings, as compared with only a few inches of the irrigated rings.

When acetylene is carried at higher pressures than 30 lb/in^2 the runs of pipe are likely to be smaller in diameter : at such pressures detonation can be set up in these narrower pipes and in much shorter runs. In the German butynediol plant, which operated at 5·5 atm abs, but not the plants operating at 20 atm, the packing of pipes with bundles of narrow tubes is featured.[13] Their purpose was to prevent deflagrations building up into detonations, since the reactors etc. into which the pipes led were designed to withstand deflagrations but not detonations.

Experiments at Griesheim[5] around 1940 suggested that such tube bundles in pipes of up to 6 in. diameter could prevent detonation if the initial pressure was not above 4 atm, but they served no useful purpose at initial pressures of 8 atm g. The present authors have confirmed the uselessness of narrow tubes at pressures above 9 atm g, because they find that at all pressures above this, detonation is set up and travels through tubes as narrow as ⅛ in. diameter.

Some data on the length of pipe needed for detonation to occur have been obtained using 100 ft runs of 1 in. pipe, by

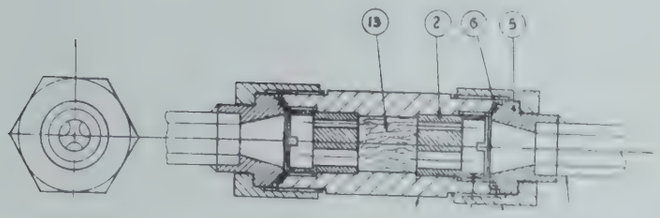

Fig. 10.—*Steel wool explosion arrestor assembly*

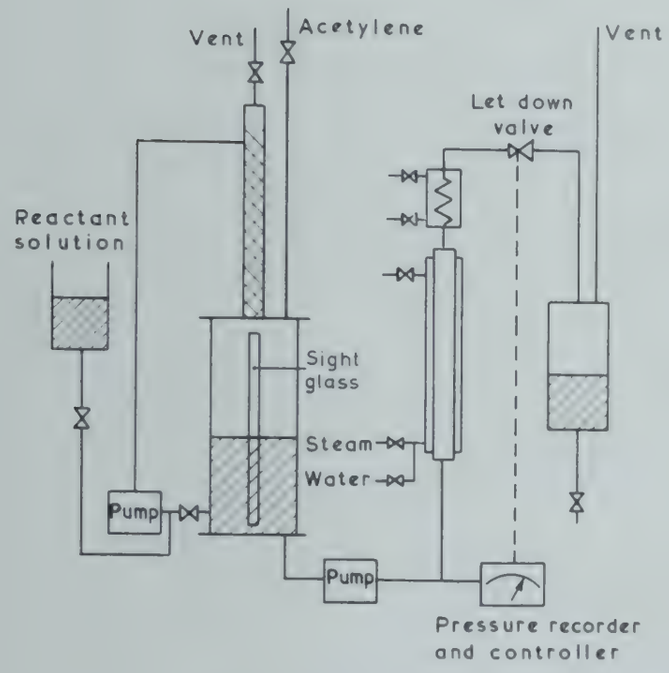

Fig. 11.—*Experimental plant for acetylene reactions at high pressure (120 atm) in single, liquid phase*

initiating explosion by fusing a platinum wire at one end. At pressures below 3½ atm abs the decomposition wave tends to die out in about 12 ft, but at all higher pressures detonation developed. The distance needed for the detonation to develop decreases markedly with rise in initial pressure. The results are given in Table III.

TABLE III.—*Length in which Detonation Develops in 1 in. Pipe*

Initial pressure (atm abs)	3·5	3·8	5·0	20·0
Length for detonation (ft)	30	22	12	2·8–3·2

It was found that bursting dics in the pipeline operated, but they do not prevent the build-up of detonation nor do they arrest or damp down detonation once it is set up.

In order to prevent detonation in a pipe (which is likely to be able to withstand it without bursting) causing detonation in attached items of plant (which have been designed to resist bursting in deflagration only) it is necessary to insert explosion arrestors between pipelines and vessels.

There have been many designs of arrestors for acetylene decompositions, mainly for use in acetylene compressing stations when filling cylinders. The explosion arrestor for acetylene decomposition is based on the usual general principle of flame arrestors, *viz.* the presentation to the path of the explosion of a large surface to remove the heat quickly from the flame front. In the case of acetylene, very fine passages have to be used in the arrestor. It has been proposed to do this by various forms of plugs of compressed powders, but many of these, whilst effective in suppressing detonation, offer very considerable resistance to the normal flow of gas.

One satisfactory form of arrestor consists essentially of sintered metal hollow cylinders,[14] the gas flowing first into an annular space between the cylinders and an outer pipe, then through the cylinder walls. The cylinders need to be supported from the inside to prevent them being crushed by the force of the explosion wave ; also they cannot always tolerate an explosion wave passing within them outwards, and therefore the arrestor has to be so constructed that an explosion coming from either direction first meets the outer surface of the sintered metal cylinders.

Other flash arrestors have been constructed from shredded metal such as steel wool. In the Reichanstalt,[5] compressed steel wool sponges were found to arrest detonations in 5 in. diameter pipe at pressures up to 6 atm. Later work at Griesheim found that in 8 in. pipe, detonations were arrested by compressed steel wool, but on occasions the explosion was re-initiated after some considerable time (up to 20 minutes), a slow flame eating its way through the steel wool packing in this period.

The authors have studied the arresting of detonation at higher pressures in a narrower pipe. Under these conditions, steel wool plugs 1 in. long compressed to a porosity of 75% have been found to be always effective in suppressing detonation. Difficulties arose through damage to the retaining perforated plates under the impact of the detonation, and such difficulties could be overcome by various mechanical devices ; one such involves an arrestor of outer diameter somewhat larger than the pipeline with a conical element in the expansion junction.[5] This attenuates the explosion wave sufficiently to avoid damaging the retention plates.

A typical assembly is shown in Fig. 10.

Very High Pressure Work

The chemical reactions for which compressed acetylene has been used or proposed are all liquid-phase, and the acetylene is compressed in order to maintain a sufficiently high concentration in the liquid for reasonable rates of reaction. Whereas liquid acetylene, especially if compressed, has been known to explode very violently, explosions in systems containing acetylene and solvents appear to occur exclusively in the gaseous phase. The reaction between acetylene and a solvent or another reactant in solution in the same solvent may accelerate very rapidly under certain conditions, but explosive conditions have not been recorded. The consequences of acceleration of reactions should be controllable by bursting discs or relief valves in conventional manner.

It has therefore been considered that if acetylene is reacted in a system in which there is only a liquid phase, much higher pressures can be tolerated.[16, 17, 18, 19]

In principle the system used is to dissolve acetylene with the other reactants in the solvent at ambient or sub-ambient temperatures, and then to pump the solution into a reactor which is maintained at the necessary temperature for reaction and in which the pressure rises to a value greater than that needed to maintain the acetylene in solution at the reaction temperature. The reacted liquid then flows through a reducing valve, so that there is no gas phase at all at the high pressure in the reactor. Fig. 11 shows the plant used.

It is not yet known whether any actual production units have been based on this principle. It has however been

applied on an experimental basis to the production of vinyl ethers from acetylene and alcohols with alkaline catalysts, to the production of *cyclo*-octatetraene from acetylene itself in solution in the appropriate solvent in presence of nickel catalysts, to the vinylation of pyrrolidine, etc. The authors have studied these reactions at up to 150 atm, the reducing valve in the reactor being set to allow reacted liquid to pass out when this pressure is reached. Explosions have never been experienced in this liquid-phase reactor, although uncontrollable slow rises in pressure have occurred which have been completely relieved by the functioning of bursting disc rated to operate at 200 atm.

Conclusions

In handling acetylene for chemical reactions carried out under pressure, the following precautions need to be taken :—

All possible sources of ignition of an acetylene-air mixture external to the plant items must be avoided. Electrical equipment should be housed as far as possible in rooms separate from places where acetylene is being handled, and any electrical equipment still remaining in places to which leakage of acetylene can penetrate should be totally enclosed, and the housing enclosing it (including conduit carrying electrical leads) should be pressurised to a few inches of water gauge with dry air.

Potential sources of ignition within the acetylene-containing system must be avoided. Reactors should never be heated by flame and, preferably, not directly by electricity, but by hot fluids. Silver in any form must be avoided, and so must copper or copper alloys containing more than 70% of copper. Even alloys of lower copper content could well be avoided where equally satisfactory alternatives exist.

Reactors and other plant items containing acetylene under pressure should be so designed that at no time is the length of the gas phase more than four times its diameter, and the item should have a test pressure 11 times the operating pressure. A suitable explosion arrestor needs to be inserted in the pipe leading into or out of the vessel, near the point of entry. As an ultimate precaution, to protect personnel against injury should all the above safety measures fail, reactors and other dangerous plant items should be installed in the open or in rooms whose roofs include a light blow-off cover, and the operators should work with an appropriate wall between them and the compressed-acetylene vessels. Instrumentation needs to be arranged accordingly.

Long runs of wide pipeline carrying acetylene at medium pressures should be buried or laid in deep trenches, and explosion arrestors be interposed between the pipeline and the equipment for feeding acetylene into it, and also for taking acetylene from it. One type of arrestor comprises a tower filled with Raschig rings.

Reactors designed and operated so as to contain the acetylene only in solution, with no gas-phase at any time, can be protected with bursting discs, without requiring the 11-fold test factor.

Acknowledgment

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THE DESIGN OF PLANTS FOR HANDLING HYDROFLUORIC ACID

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SUMMARY

The paper discusses the special problems in the design of process plant for handling hydrofluoric acid. Standards of containment superior to those normally applied to industrial acid uses are not required but such standards are difficult to achieve because of corrosion problems. Caution is necessary in using corrosion data obtained from the literature and welding can present problems.

Introduction

In recent years the use of fluorine derivatives has increased considerably. Until lately, when elemental fluorine has become available, this has generally involved the use of hydrofluoric acid.

The first large scale use in a modern process outside the metallurgical industries was the Phillips alkylation process. This came into prominence during the war, and because of the state of emergency a considerable amount of data was released.[1] This data still forms the most useful source for essentially anhydrous systems in the presence of organic materials.

The useful properties of uranium tetrafluoride and hexafluoride has inevitably resulted in these compounds playing a fundamental part in nuclear fuel processing. Their production has entailed high temperature processing with hydrofluoric acid, fluorine, and other fluorinating agents. The present paper is concerned with the use of hydrofluoric acid in this field.

Hazards Associated with Hydrofluoric Acid

Hydrogen fluoride (HF) both in the anhydrous state and in solution in water is a very reactive chemical. It is not, however, particularly prone to reactions of explosive violence.

The hazards in handling hydrogen fluoride are associated with its toxicity and its ability to produce severe burns. Containment is therefore the primary problem, and this is made more difficult by its corrosive nature.

Anhydrous hydrogen fluoride boils at 19·54°C at atmospheric pressure and, in consequence, reactions at moderate temperatures utilising the liquid phase require pressurised equipment. Its low heat of vaporisation, *circa* 1950 cal/mole for pressures above atmospheric, makes it possible that large volumes of vapour will be released in the event of a burst in a pressurised system. This problem reduces rapidly in magnitude as the concentration in aqueous systems is reduced to that of the azeotrope at 37·5% HF, boiling at 112·4°C at atmospheric pressure.

The toxicity of hydrogen fluoride is evidenced both in direct effects and to a lesser extent in the long term effects of fluorides generally. Breathing hydrogen fluoride vapour causes pain and damage to the respiratory system ; breathing of small amounts of very dilute gas for a short period is unpleasant and possibly painful, but is not likely to cause permanent damage.

Table I represents conditions under which it is believed that nearly all workers may be repeatedly exposed day after day without adverse effects. The values are time-weighted average concentrations over a normal working day. Values for a number of gases are shown in the table for comparison.

TABLE I.—*Exposure Threshold Limit Values*

Gas	p.p.m.	mg/m³	Ref.
HF	3		2
Fluoride/Dust	—	2·5	2
F	0·1		2
HCl	5		2
Cl	1		2
HCN	10		2
SO_2	10		3
SO_3	2		3

It has been found that hydrogen fluoride vapour can be detected by most people in concentrations as low as 2 p.p.m. by its smell. At levels of 60 p.p.m. the vapour is intolerably irritant on breathing, and concentrations of 50–250 p.p.m. cause damage to the lungs. As a design figure, therefore, 10 p.p.m. should be regarded as a maximum for brief exposure in an emergency.

Fluorosis resulting from inhalation of fluoride dusts is a form of sclerosis (stiffening) of the bones due to fixation of calcium, and takes some years to develop. The risk of fluorosis from hydrogen fluoride is considered slight, but of course any plant handling hydrogen fluoride is also likely to be handling fluorides and the problem must be taken into account.

Contact of liquid hydrogen fluoride with the skin causes burns which are very painful and can cause serious permanent damage to the tissue. The wounds are exceptionally slow in healing.

Acid of over 60% strength will cause immediate apparent damage and pain, but in the case of contact with acid below 20% strength the appearance and pain may be delayed for some hours. Contact with the eyes is particularly dangerous and can cause blindness.

Corrosion in Systems Containing Liquid Hydrogen Fluoride

The available corrosion data for hydrogen fluoride has now grown to considerable proportions, but much of it refers to

* United Kingdom Atomic Energy Authority, Risley, Warrington, Lancs.

particular conditions and is not widely applicable. Many of the reported data have been obtained in tests of short duration and this casts considerable doubt on their significance ; great care must be exercised in their application. The additional data presented in this paper are also restricted in their use, but it is hoped that by defining the conditions an additional relevance may be given them.

The data concerned in this section of the paper have been obtained for the design and from the operation of the hydrofluorination reactors and the hydrogen fluoride rectifying unit attached to the experimental fluidised bed unit for the production of uranium tetrafluoride at Springfields. It is therefore relevant to consider the flow diagram of the plant shown in Fig. 1.

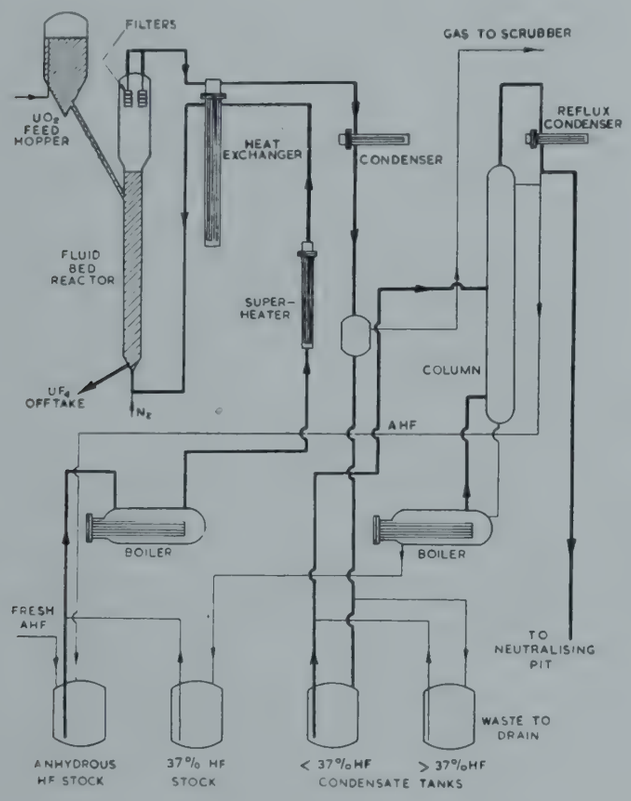


Fig. 1.—*Production of uranium tetrafluoride*

The process has been described in detail by Hawthorn, Shortis, and Lloyd.[4] Uranium tetrafluoride is obtained by decomposing uranyl nitrate to uranium trioxide, followed by reduction with hydrogen to uranium dioxide, which is then converted to uranium tetrafluoride with hydrofluoric acid gas in a fluidised bed reactor.

$$UO_2 + 4HF \rightarrow UF_4 + 2H_2O$$

The reaction is currently carried out batchwise at temperatures between 200 and 450°C giving a tail gas varying in composition from 0% HF at the beginning of the reaction to 100% HF at the end.

Hydrogen fluoride vapour is generated in a boiler and after passing through a superheater and heat exchanger, is used to fluidise the bed of uranium dioxide, with nitrogen being added as required. The tail gases leaving the bed pass through filters and the heat exchanger before passing to a condenser which removes water and residual hydrogen fluoride. The condensate is segregated into hydrogen fluoride above and below the azeotrope strength.

The hydrogen fluoride is recovered in a simple rectifying plant, hydrogen fluoride of azeotrope strength being recovered from the still bottoms and either water or anhydrous hydrogen fluoride from the column top, depending on whether the feed was below or above azeotrope concentration. The recovered azeotrope may be used to feed the reactors during the early part of the reaction.

The generally accepted materials of construction for plants handling liquid hydrogen fluoride of concentrations greater than 75% are Monel and carbon steel. The latter gives satisfactory resistance in the cold and may in some cases be more economical than Monel for hot hydrogen fluoride. For concentrations lower than this Monel and copper have given satisfactory performance in different plants. Stainless steels in general are unsatisfactory for all concentrations.

Silver is also a satisfactory material of construction for hydrogen fluoride plants and possesses superior resistance in the presence of oxygen and oxidising agents. Magnesium alloys are also resistant to hydrogen fluoride under slightly oxidising conditions, but their use is yet undeveloped. Trials are being carried out with Magnox, the fuel element canning alloy.

The corrosion rates of all these materials are considerably influenced by the presence of air, oxidising agents, agitation, and trace amounts of other materials. Recent work on the re-processing of zirconium and stainless-steel clad nuclear fuels has involved the use of strong oxidising agents with dilute hydrogen fluoride, to dissolve these alloys. No truly resistant material has been found, but alloys such as Monel have given moderate resistance in the presence of nitric acid and chromates. Carpenter 20 and some stainless steels have also given reasonable performance provided welds are avoided. For use with hydrogen peroxide/hydrogen fluoride solutions, Hastelloy C shows some resistance. The anhydrous system NO_2/HF is resisted adequately by Monel.

For the Springfields plant it was decided to use Monel for parts handling liquid hydrogen fluoride except for the storage of cold anhydrous acid where carbon steel was used. A number of straightforward corrosion tests were carried out and the results are shown in Table II.

TABLE II.—*Laboratory Tests on Monel Specimens in Boiling* 40% *Hydrofluoric Acid* (130°C) *with a Hydrogen Blanket*

Vol % O_2 in purge gas	Penetration rate (mm/yr) Liquid	Vapour
0	0·29	0·027
0·1	0·54	0·048
1·0	1·92	0·30
Air Blanket	0·55	25·6

The specimens included radiographed argon arc welds with Monel 60 wire and no preferential attack was noticed on the welds.

Design was based on oxygen contents of less than 0·1% in gas streams.

It has been reported in the literature that Monel is easy to weld and that since it is a solid solution type alloy the welds are homogeneous. In practice considerable difficulty in producing sound welds has been experienced during the construction of the Springfields Plant.

The standards decided on were virtually the same as had been used successfully with stainless steel on the Windscale plants. These are rather more stringent than Lloyds Class I. It was soon found that the technique had to be considerably different.

For plates thicker than $\frac{1}{4}$ in. it was found that metal arc welding with fluxed Monel 130 or 140 electrodes gave satis-

factory results. For thinner plates the best results were obtained by forming an internal bead run made with an argon arc torch using unfluxed Monel 60 electrodes, the weld then being filled with metal arc 130 or 140 electrodes. Attempts to carry out the initial run by fusing the plates with argon arc produced highly porous welds. Careful weld preparation and absolute cleanliness had to be observed during welding.

The vessels were not designed for full radiography, although butt welds were used where it was possible without undue expense.

TABLE III.—*Monel Piping—Specification U.K.A.E.A.(I.G.) 70591. Material to B.S. 1532, fully annealed*

Bore (in.)	Outside dia. (in.)	Wall Thickness s.w.g.	Wall Thickness (in.)
1	$1\frac{11}{32}$	14	·080
2	$2\frac{3}{8}$	12	·104
3	$3\frac{1}{2}$	10	·128
4	$4\frac{1}{2}$	—	·250

The piping used is thin-wall to U.K.A.E.A. standard (see Table III). This was found to be very difficult to weld. The most satisfactory technique found was argon arc welding with Monel 60 wire. It was found essential to radiograph the welds since bad porosity could occur in welds which had no unacceptable visual defects. Fig. 2 shows an extreme example of this kind of porosity. Approximately 80% of the early welds which passed visual inspection were later rejected on radiographic examination, although with increasing practice the percentage of faulty welds has now been reduced to normal proportions. Careful weld preparation and absolute cleanliness are even more important than in the case of plate, and it was found essential to exclude air draughts which could temporarily deflect the argon shielding.

The corrosion experienced on the plant during initial operations is indicated by the results in Table IV.

The results covered in the table can be divided into three periods during which operating conditions were different,

Fig. 2.—*Section through an argon arc/Monel 60 electric weld showing serious porosity with no external or internal visuals defects—1 in. N.B. pipe*

particularly with respect to the oxygen content of the process gases.

During period I the plant was being frequently shut down for mechanical checks, thus allowing ingress of air and occasional oxygen contents as high as 5%. It was found in practice that the oxygen content did not fall below 0·1%. The corrosion rates experienced during this period were in line with the rates determined in the laboratory tests as in Table II, when allowance is made for the variable oxygen content. It was therefore decided to introduce hydrogen into the feed gas

TABLE IV.—*Plant Corrosion Rates*

Specimens suspended in plant

Unit	Period	Approximate acid strength	Temperature T°C	Oxygen content	Exposure Time At T°C (h)	Exposure Time Total (h)	Mean Corrosion Rate Penetration (mm/yr.) Liquid At T°C	Liquid Total	Vapour At T°C	Vapour Total
Boiler	I	40%–80%	80°C–150°C	0·1–0·5%	656	762	1·4	1·2	2·7	2·4
	II	40%–80%	80°C–150°C	100 ppm	—	450	—	10	—	10
	III	40%–80%	80°C–150°C	<100 ppm	39	226	8·0	1·4	1·2	0·2
Boiler	I	80%–100%	50°C–80°C	0·1–0·5%	129	241	0·24	0·13	0·3	0·16
	II	80%–100%	50°C–80°C	100 ppm	428	543	0·05	0·04	0·08	0·06
	III	80%–100%	50°C–80°C	<100 ppm	1248	1393	0·09	0·08	0·06	0·05
Boiler	I	40%–80%	50°C–112°C	0·1–0·5%	570	770	0·4	0·3	0·8	0·6
	II	—	—	—	—	—	—	—	—	—
	III	40%–80%	50°C–112°C	100 ppm	292	1080	0·5	0·13	0·6	0·16
Condensers :	I	10%–100%	80°C–150°C	0·1–0·5%	—	277	—	1·4	—	—
Inlet ..	III	10%–100%	80°C–150°C	<100 ppm	—	330	—	0·6	—	—
Outlet ..	I	—	20°C	0·1–0·5%	—	400	—	—	—	0·33
Distillation :										
Column										
Top ..	I	100%	20°C	0·1–0·5%	—	230	—	0·6	—	—
Bottom ..	I	38%	112°C	0·1–0·5%	—	230	—	2·2	—	—
Heat exchanger :										
Shell ..	I	70%–100%	Approx 200°C	0·1–0·5%	—	420	—	—	—	0·1
Tube ..	I	70%–100%	Approx 200°C	0·1–0·5%	—		—	—	—	0·4
Superheater ..	I	70%–100%	190°C	0·1–0·5%	—	970	—	—	—	0·4
	I	100%	190°C	0·1–0·5%	—	129	—	—	—	0·1

to the reactor to reduce the oxygen level. This was successful and combined with less opening up of the plant enabled levels of 100 p.p.m. to be maintained continuously during period II. It was therefore somewhat surprising that the corrosion rates increased in some vessels as high as 10 mm/yr. during this second period.

Results in the third period have generally been similar and the oxygen content was further reduced to less than 100 p.p.m.

Despite the evidence from the initial corrosion tests that no preferential attack occurred at welds, a number of welds failed in practice in the course of all the periods and it was evident that some preferential attack on welds was taking place. It should be emphasised that some of the corrosion rates experienced were sufficient to account approximately for a number of failures in thin-walled piping, but the fact that the failures were, with few exceptions, associated with welds, made it desirable to investigate weld corrosion further.

A careful examination of the radiographs taken at the time of welding showed that a number of welds which subsequently failed had marginal defects. It was also found that the list of failed welds contained rather more cases where, in order to secure a sound weld, cutting and re-welding had been required. A corrosion programme on welded specimens was therefore begun, this being carried out in more refined apparatus which had been developed during the course of the corrosion programme. This apparatus gave extremely accurate control of the oxygen content and adequate stirring ; additionally, extreme care was taken in the preparation of the samples, these being cut from the middle of plates of a thickness appropriate to the type of weld being tested. Tests were made on welds carried out by argon arc with Monel 60 filler, and with metal arc Monel 130 and 140 electrodes. Initial results indicate that the Monel 130 weld is cathodic compared with parent metal, whereas Monel 60 is slightly attacked preferentially to parent metal, and Monel 140 is attacked more severely. Figs. 3 and 4 show samples. It is yet too early to say whether the cathodic form of the 130 weld results in undercutting of the weld, although there is no sign of this to date.

Further work has indicated that undercutting of the weld does not take place. Also included in the programme were a number of re-welds, but results are not yet available on their performance.

Not included in the tabulated data is the performance of Monel and Inconel in the reactor proper, which has been exposed to gaseous hydrogen fluoride at temperatures up to 450°C ; here the corrosion has been slight and performances is satisfactory.

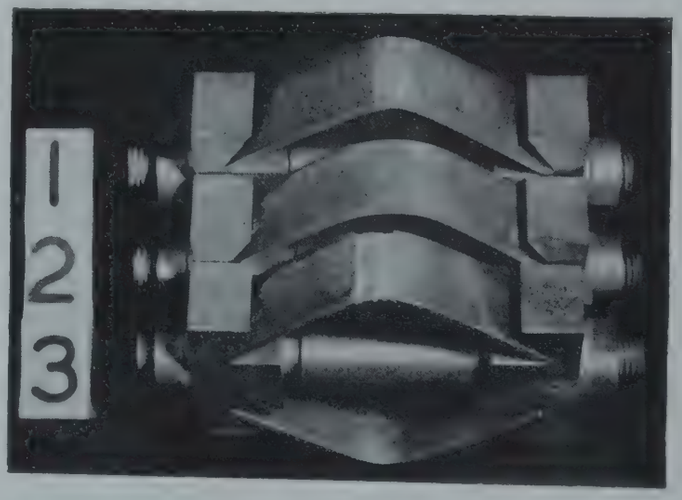
It is noticeable that the severe corrosion is associated with intermediate strengths of liquid hydrogen fluoride at higher temperatures.

Increased corrosion rates have been experienced at the entrances to heat exchangers which are evidently due to the condensation of acid during the heat-up cycle, and severe pitting of tubes has resulted. Parts fabricated from bar-stock have suffered severe end-grain attack and this type of construction should be avoided.

Plainly, factors other than oxygen content affecting corrosion have entered into plant operation. Nitric acid has been found to be present in the recycled hydrofluoric acid at up to 20 p.p.m. and it would seem likely that higher levels might occur locally. Sulphuric acid is added to the uranyl nitrate entering the process and traces of sulphide and sulphate have been found in the recovered hydrofluoric acid. It is thought that the sulphate does not materially effect the corrosion, but testing is being carried out on the effect of small quantities

1 — argon arc/Monel 60 weld
2 — metal arc/Monel 140 weld
3 — metal arc/Monel 130 weld

Fig. 3.—*Liquid-phase corrosion of Monel welds (plan view) in 40% hydrogen fluoride at 70°C after 1000 hours exposure with 1% oxygen atmosphere*



1 — argon arc/Monel 60 weld
2 — metal arc/Monel 140 weld
3 — metal arc/Monel 130 weld

Fig. 4.—*Liquid-phase corrosion of stressed Monel welds in 40% hydrogen fluoride at 70°C after 1000 hours exposure with 1% oxygen atmosphere*

of nitric acid. The present results indicate that levels of 20 p.p.m. HNO_3 give only a moderate increase in the corrosion rate, but levels of 100 p.p.m. might cause increases of the same order as experienced in some sections of the plant. It is possible to postulate reasons for fluctuations in the nitric acid content which could cause the increase in corrosion between period I and period II.

Sulphide corrosion has definitely been experienced in the condensers, where deposits of essentially copper sulphide have been found on the tubes. It seems probable that the sulphide content of the gases is virtually completely removed here.

Design Considerations

It has been shown that hydrogen fluoride is not intrinsically more toxic than many other industrial chemicals, and that provided an equivalent standard of containment can be established, hydrogen fluoride can be handled just as readily.

The first consideration in the design of any plant handling hydrogen fluoride is thus that of coping with corrosion. Much can be done in considering the basic process to be operated. If this can be arranged so that intermediate strengths of hydrogen fluoride, *i.e.* $<70\%$ and $>20\%$, are not handled, the problem is much simplified. If the reactions can be carried out in the vapour phase, well above the dew point, corrosion will again be much less.

When these points have been considered the effect of leaks on both plant operation and safety must be assessed.

If the amount of hydrogen fluoride that can be released from a failure is small and would not constitute a hazard away from the plant itself, it is reasonable to consider an open-type plant. This might arise in the case of small low pressure plants with low liquid hold-up. In general, however, if the corrosion conditions to be expected are severe, *e.g.*, as might arise with intermediate strength acid, the amount of maintenance work will be high and in this country an enclosed plant may be necessary. The same enclosure may be utilised to contain any leaks which may occur since in general, maintenance of this type of plant is not practicable during operation.

The enclosed cells must be adequately ventilated to a scrubber capable of dealing with the largest leak likely to occur.

Air changes should be such that with minor leaks, maintenance workers can enter without air lines ; in these circumstances the air entering the scrubber will be below breathing tolerance and hence will be virtually free of hydrogen fluoride on leaving. Under major leak conditions, however, the scrubber should be capable of reducing the concentration of hydrogen fluoride to 10 p.p.m., thus ensuring that there is no hazard to surrounding areas.

In both open and enclosed plants the operation should be remotely controlled from control rooms supplied with fresh air. In open plants, stop-valve operation would be direct, but all valves and flanges should be shielded as a protection against acid spray ; this precaution is also advisable to protect maintenance personnel in an enclosed plant. Entry into open plants inevitably involves a clothing change as must entry into the cell area of an enclosed plant ; it is therefore an advantage in an enclosed plant to have as many of the manual valves as possible operated by means of extension spindles through the enclosure walls.

In designing both open and enclosed plants rather more care than usual should be devoted to providing easy and safe exits. Platforms should have wide passage ways and exits at each end ; in the case of cells, doors should be provided at each end leading to external stairways, duplicated internally where desirable. As far as possible cells should be similar in layout so that in the event of a leak personnel will have no hesitation in taking the correct way out.

The usual provisions for emergency treatment equipment must be made with warm water showers, eyewash bottles, etc., at regular stations.

Sprays have been installed in the cells of the Springfields plant, so that a major leak could be killed quickly, and to ensure that any pockets of acid accumulated on platforms, steelwork, etc., have been thoroughly diluted and washed down. Without this precaution it could be hazardous to enter a cell after a major leak.

An important feature of both process and plant design must be the elimination of oxidising agents and dissolved oxygen. If this can be achieved the corrosion problem becomes reasonable. Inert gas blanketing is therefore essential, nitrogen being commonly used for this purpose.

A consequence of this is that processes should be continuous. The large changes in composition associated with batch processes make the control of corrosion difficult and the similar changes in the amounts of material in vessels make the control of oxygen contents difficult even though inert gas blanketing is practised.

For anhydrous hydrogen fluoride carbon steel is the natural choice with Monel being used where there is possibility of dilution to 70% or where temperatures are above about 50°C. For cold dilute and intermediate strengths of hydrogen fluoride polythene and polypropylene should be given serious consideration. It is probable that hard rubber, neoprene, and butyl rubber would also be satisfactory for this service.

For hot intermediate strengths the choice is between Monel, silver, and magnesium alloys. The particular conditions of the process to be used will determine this choice. In the case of Springfields plant it is not yet possible to say which is the most economic. In both cases the design of equipment should be of the simplest ; in the case of Monel this is to reduce the number of welds and make it possible to radiograph them all ; in the case of silver to facilitate lining.

It can be seen that all factors affecting corrosion come into the fundamental decision as to whether to have an enclosed or an open plant.

Although an enclosed plant is considerably more expensive, it is reasonable to consider that where enclosure is necessary this extra cost is merely a reflection on the state of development of the process and has its compensations in reducing the operating costs of such under-developed processes. Thus a highly-refined continuous process with small in-process hold-ups, and one that avoids the more corrosive conditions and hence can be as safely built as an open plant, is likely to have a small operating staff and a high on-stream time ; by contrast, a less well-developed batch-process with large hold-ups and severe corrosion problems will have a much larger operating staff. Under the latter conditions the savings in process labour due to elimination of change times and the ability to go on operating the plant in safety with quite considerable leaks can obviously lead to economies to offset the cost of enclosing the plant.

For both types of plant a high standard of construction is essential for economic as well as safety reasons. The tendency of Monel to give porous welds undetectable by visual inspection demands the highest standards of radiographic inspection.

Mechanical Design

It has already been mentioned that design of vessels should be simple and, if in Monel, should be capable of radiographic inspection. Vessels holding liquid and, in particular, stock tanks, should not have bottom outlets.

The attachment of branches to vessels is difficult and should be avoided if possible by the use of alternative designs, *e.g.* coils rather than tubular heat exchangers with headers.

Fillet welds have not been eliminated in the Springfields plant, but care has been taken to provide full penetration welds with a reinforcing plate.

An alternative preparation which could be considered is that shown in Fig. 5. This has been used extensively on stainless steel at Windscale and can be satisfactorily radiographed.

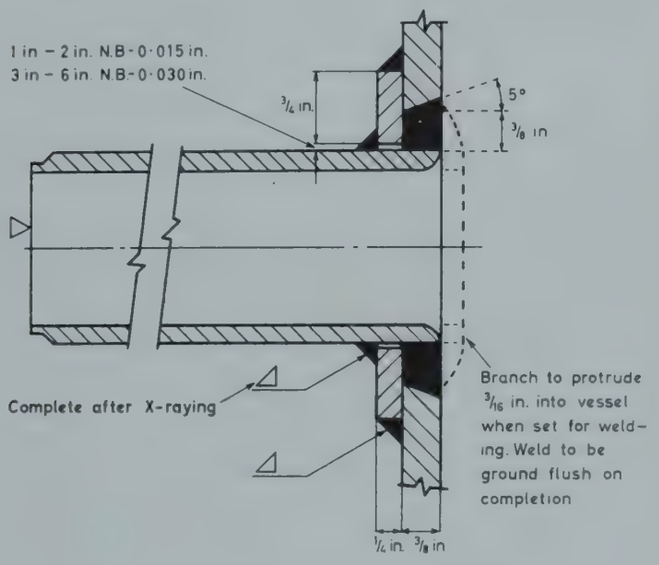

1 in – 2 in. N.B - 0·015 in.
3 in – 6 in. N.B - 0·030 in.
3/4 in.
5°
3/8 in
Complete after X-raying
Branch to protrude 3/16 in. into vessel when set for welding. Weld to be ground flush on completion
1/4 in.
3/8 in

Fig. 5.—*Branch weld preparation*

Forged weld-neck flanges should be used exclusively.

Allowance should be made in the design of vessels for accelerated corrosion rates. Thus at the Springfields plant the vessels were designed for a test pressure of 250 lb/in^{2}g and a working pressure of 100 lb/in^{2}g with an additional allowance of corrosion at the anticipated rate of 0·5 mm/yr.

Since the actual working pressure is 50 lb/in^{2}g, an adequate margin for accelerated corrosion between inspection periods has been obtained.

Piping should be designed to eliminate as many welds as possible and should be fully radiographed. Corrosion with hydrogen fluoride is reportedly velocity-sensitive,[1] and hence pipes should be of ample bore.

Forgings should be used for flanges, valves, and other fittings since sand castings in Monel have proved very porous and have almost all been failures.

Where carbon steel fittings are used with anhydrous hydrogen fluoride, the use of Monel trim is advisable.

Three satisfactory methods of flange jointing have been found in the Springfields plant, but others would certainly work.

Because of the high temperatures at the reactor, a metallic joint was chosen and Monel and Inconel lens rings have proved satisfactory. These were subsequently used throughout the experimental plant. The importance of using rings of the same composition as the parent flange metal must be emphasised. Severe electrolytic corrosion takes place in the presence of liquid hydrogen fluoride if slightly dissimilar metals are used.

Spiral packings of interleaved Monel and P.T.F.E. trapped between flat flange faces have also proved satisfactory up to 200°C.

For low temperature service P.T.F.E.-enveloped asbestos packings have been proved suitable.

Whilst there is no fundamental objection to the use of glanded pumps in hydrogen fluoride service, Springfields experience is not encouraging. Carbon has not proved successful as a rubbing contact in hydrogen fluoride and it is consequently difficult to find a suitable pair of rubbing surfaces for mechanical seals on pumps. Work is still continuing on this.

P.T.F.E. is not in general a suitable gland packing for high-speed shafts and consequently the simple type of centrifugal is not used at Springfields.

Double diaphragm pumps are used for boiler feeds ; a glandless extended-spindle centrifugal is being developed at the Capenhurst laboratories which should prove a more satisfactory long-term answer.

Air-operated control valves used at Springfields have bellows seals made from Monel with a P.T.F.E. laminated safety packing. The bellows have been subject to stress corrosion, and since they are inevitably thin, their life has been short. The edge-welded type of bellows which is the most satisfactory in stainless steel is less so in Monel for hydrogen fluoride service since the metal is attacked adjacent to the welds : the convoluted type is preferable. At Springfields many of these valves are located on filter blow-back units of the fluidised bed and here the corrosion has been substantially reduced by heating the bellows to ensure that condensation cannot take place.

Safety valves are protected by bursting discs. Careful location of these can usually ensure reasonable replacement times.

Operational Experience at Springfields

The experimental plant from which experience has so far been gained has been built with reactors in an existing building and the boilers and hydrogen fluoride recovery plant in an adjacent open structure. The reactors are the core of the process and most of the effort has been expended on these. Since the reaction is at high temperature, they are constructed of Inconel and no substantial corrosion problems have been met. In consequence of the development programme on the reactors, most of the experience in hydrogen fluoride handling has come from the boiler and feed systems, these having operated both on azeotrope concentrations and on high strength hydrogen fluoride and the condensation systems which have operated at all concentrations.

It has been found anew that even a small proportion of failures can cause serious disruption to a programme ; however, with experience it has been found possible to tolerate small leaks.

Fairly extensive arrangements for detecting leaks were installed but they proved unnecessary. The nose is far more sensitive and specific. Small leaks have been adequately dealt with by hosing with water and neutralising with soda ash. The visible fume from a leak serves as an adequate warning to plant personnel.

Repairs by patching leaky welds have proved totally unprofitable and it has in general proved better to insert a new piece of pipe with the welds located in convenient positions. Decontamination of the plant for repairs has

proved remarkably easy. For low strengths of hydrogen fluoride, washing out with water is adequate. For anhydrous hydrogen fluoride, where water cannot be used, draining followed by nitrogen purging removes the hydrogen fluoride rapidly. The times taken to do this in vessels are naturally longer, but the process is effective.

Experience gained in the use of protective clothing confirms that of other users. In control rooms and other non-contact areas normal plant overalls are used. For any inspections and valve operation in the plant area, *i.e.* that portion which in the new plant will be in the cells, operators wear face shields and gloves in addition to normal overalls. In the event of a suspected or known leak of considerable magnitude operators entering the cell wear a polythene suit with hood and self-air mask. Fitters are similarly clad for emergency maintenance, *e.g.* to tighten a leaking valve gland with the plant under pressure. Fitters also wear a polythene suit, hood and self-air mask when starting to strip down plant which has been purged. As soon as it has been ascertained that no pockets of hydrogen fluoride remain, they revert to normal overalls, eye-shields and gloves.

The amount of maintenance possible with the plant on-stream has grown with experience. Control valves positioned between isolating valves and fitted with a manual by-pass are now replaced without shut-down or purging, fitters using the clothing described above. In general those maintenance operations involving a small release of hydrogen fluoride can be safely completed.

Conclusions

The toxicity of hydrogen fluoride is comparable to that of many other industrial gases, but its burning effect, in liquid form, is more severe than that of most acids. It can readily be detected by smell at its safe working exposure-level and leaks of all but dilute acid are readily located visually by the fume.

In consequence, the design of safe plant does not require standards of containment in excess of those normally applied to industrial processes using acids. The measures required to achieve satisfactory containment are functions of the process design and state of development. With present knowledge, plants handling large volumes of hydrogen fluoride at its boiling point under moderate pressures should have secondary containment cells if there is any possibility of high corrosion rates.

Confidence gained from operations at Springfields indicates that further plants could be built in the open with suitable modifications to the larger hold-up vessels and with the improvements expected in the process.

Corrosion rates of Monel and Inconel by gaseous hydrogen fluoride of all concentrations are low at temperatures above the dew point, and plant design does not present new problems. Corrosion rates of Monel by liquid anhydrous hydrogen fluoride are low, but are accelerated in the presence of small quantities of oxidising agents, but even so they are still tolerable and do not present severe problems. Intermediate strengths of hydrogen fluoride give reasonable corrosion rates, but in the presence of small amounts of oxidising agents the rates increase rapidly and become severe. Operating experience indicates that under plant conditions the rates can be accelerated further.

Caution should be exercised in the use of corrosion data on Monel from the literature : much of this data is on tests of inadequate duration.

Satisfactory welding of Monel is difficult. For thin-wall piping, argon arc welding with Monel 60 electrodes is the most satisfactory method and for plate, metal-arc with Monel 130 electrodes. Monel plants demand high standards of construction, and design should be such as to allow for radiographic inspection of welds both in vessels and pipework. Failure to do this is likely to result in a plant with exorbitant maintenance costs and doubtful safety.

Careful attention to detail design is required since there are few satisfactory solutions to problems of sealing static and moving joints. Operating experience shows that reasonable flexibility in the toleration of small leaks is practicable provided that first-aid measures are taken and personnel are correctly clothed.

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THE STORAGE AND TRANSMISSION OF HAZARDOUS LIQUIDS

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SUMMARY

The authors discuss in general terms the methods of combating some of the hazards involved in handling dangerous liquids.

Introduction

It is desirable at the outset to clarify the meaning of " hazardous liquids " in this context. The materials of which the authors have experience and which they regard as hazardous include molten lead, mercury, chlorine, bromine, sodium, caustic soda, sulphuric acid, hydrochloric acid, ethyl chloride, ethylene dibromide, ethylene dichloride, and tetra-ethyl lead. It is obvious that the hazards are not the same with all the fluids. Analysing the difference leads to the suggestion that four types of hazards exist, *i.e.*

1. Toxicity
2. Skin burns
3. Explosion and fire
4. Corrosion.

A fifth classification would be that of radiation, but this is excluded because the authors have no experience in this field.

The difference in overall hazard from one material to another arises from the fact that the relative importance of the individual hazards varies. For instance, molten lead can give off toxic fumes and can cause skin burns, but it is not likely to give rise to any explosion risks. Tetra-ethyl lead is highly toxic but not likely to cause skin burns.

If, having analysed the hazards arising from any given material into these categories, one could apply firm rules for combating each hazard the designer's task would be easy. However, generalising is dangerous and may either lead to inadequate safety or uneconomic design. Having warned of the dangers of generalisation, the authors offer the following suggestions for combating the various types of hazards.

The first is that unless it is absolutely essential, toxic materials should not be stored or pumped. If possible, it is better to feed the material directly into the next process and convert it into a less hazardous material. For instance, where bromine is produced for the formation of ethylene dibromide, the bromine should be fed directly into the ethylene dibromide plant with the minimum of buffer capacity. Another suggestion is that vapours of the toxic liquid should be kept out of the atmosphere. Tanks should be enclosed and any vents should be scrubbed or led to a point away from any personnel. To avoid vapour-laden air being emitted when tanks are being filled, the vents can be connected back to the vessel from which the tank is being filled. One method of keeping the vapour concentration down in the vapour space in a tank is to float a layer of non-toxic liquid on top of the toxic material if an immiscible non-volatile liquid can be found.

When designing tanks for liquefied gases some assistance may be obtained from D.S.I.R. Gas Cylinders and Containers Committee report, entitled *Revised Recommendations for Welded Containers for the Commercial Transport of Chlorine, Phosgene, Ammonia and Sulphur Dioxide in the Liquified State*.[1] Further information on filling ratios is given in B.S.1736 : 1951.[2] These recommendations relate to transport containers but the information can be used for static installations. No pressure relief devices are called for by these recommendations but, on static installations, it may be desirable to incorporate a safety vale. In order to prevent seepage through safety valves it is common practice to back-up the valve with a bursting disc.

Making absolutely sure that highly toxic materials are completely contained can be expensive and it may be economic to control the vapours after escape by ventilation. If this is done it is necessary to know the maximum allowable concentration (M.A.C.) in the air which a person may breathe safely for a limited period of time. M.A.C. values used for industrial purposes assume exposure of eight hours per day for a five-day week and are expressed in parts per million by volume for gases and milligrams per cubic metre for particulates. The latter is sometimes expressed in milligrams per 10 cubic metres, the volume of air breathed by a man in eight hours being approximately 10 cubic metres.

When designing ventilation systems it is good practice to employ tailored ventilation at all anticipated points of leakage such as pump glands, etc. The shape of hoods and air velocities required for adequate entrainment of escaping material will depend upon the form of emission and the characteristics of the material. Brandt[3] gives detailed recommendations for designers in this field. In enclosed buildings, any tailored ventilation system should be supported by general ventilation in order to prevent formation of stagnant air pockets where toxic materials may build up. It is desirable for the air extract system to have a capacity slightly larger than the heated air supply system so that a depression is maintained to prevent escape of contaminants to atmosphere.

In addition to keeping the vapour out of the atmosphere it is essential to keep the toxic liquid out of public sewers in the event of spillage. One method used towards this end is to surround the tank by means of a bund wall. Bunds should be constructed of or covered with non-absorbent material to ease decontamination. When designing bunds it is necessary to make arrangements by means of which the fluids can be

* The Associated Ethyl Company Ltd., Ellesmere Port, Cheshire.

reclaimed. This is often effected by a valved outlet to special chemical drainage system feeding back to a recovery plant or effluent treatment plant. If bunded tanks are installed outdoors, facilities must also be provided for removing storm water by providing a valved outlet to the normal storm water drains, usually via an interceptor. Bunds are, of course, designed to retain liquid after it is spilled. All precautions should be taken to see that spillage does not occur. To this end it is essential that the operator is provided with adequate and reliable means of knowing what is in the tank. A complete paper could be written on the subject of level indication but in this paper only one general comment will be made. Storage tanks for toxic materials should contain the minimum of equipment which will require maintenance. Any equipment which has to be removed for maintenance will add to the risk of air pollution.

Pumping toxic materials need not always be a problem. The use of glandless, canned-motor pumps or magnetic drives is frequently possible. In other cases vertical spindle pumps, arranged with extended spindle and casing so that these extend above the maximum liquid level in the feed tank, can be used. In this case a labyrinth gas seal is fitted above the liquid level and a distance piece between the seal and the combined thrust and journal bearing above the seal forms a chamber which is evacuated by connection to the ventilation extract ducting or a free vent suitably located. Transfer by vacuum or compressed air is often used, although this increases the problem of contaminated vents.

Piping can be conventional and the modern technique of all-welded lines has advantages in that it reduces the maintenance of joints. All lines must be self-draining to prevent liquid being trapped at low points because this can cause considerable air pollution if the lines are broken for maintenance. In some cases it may be desirable to install facilities for back washing the lines.

All these points of design should be backed up by a well-equipped safety organisation. The atmosphere should be monitored to ensure that concentrations above the M.A.C. are not reached. Air masks, protective clothing, and chemicals for decontamination should be readily available. Bathing facilities must be immediately to hand where toxic materials which can be absorbed through the skin are being handled.

Finally, care should be taken that the design meets the requirements of the Factories Act 1959[4] and the Alkali etc. Works Regulation Act 1906[5]. Also compliance with any Local Authority bye-laws and regulations must be ensured.

Skin Burns

Skin burns may be thermal or chemical. Thermal burns differ from the other hazards referred to in this paper in that they can occur when the hot liquids are completely enclosed in vessels and piping. However, adequate lagging can overcome this hazard and this precaution is seldom forgotten because of the need to conserve heat. Leakage of hot liquid can also be a problem and in this connection tanks and piping should not be installed over areas frequented by operators unless precautions are taken to retain spillages.

For chemical burns the liquid must contact the skin and in consequence leakage should be eliminated. Overhead installations should be avoided if possible. Joints in pipework should be kept to a minimum and an added safeguard is to wrap the gap between flanges and other potential points of leakage with suitable material to prevent any escaping fluid forming a jet which may hit passing personnel. Typical examples are the use of lead for wrapping joints in sulphuric acid lines, mild steel strips for caustic soda lines and rubber backed by steel for hydrochloric acid lines. This precaution can also reduce the risk of accidents when joints are being broken for maintenance. Drain and sampling connections should be run to safe points for disposal and where the latter are concerned protection for the operator's face should be provided. Drains taken to gulleys should be arranged to enter the gulley and to discharge without splashing.

The precautions against skin burns are basically common sense and in consequence little is said on this subject. However, in 1958, out of a total of 5869 accidents in the chemical industry, 527 were due to injuries from molten metal and other hot or caustic substances.[6] There would appear to be a need for a more rigorous application of common sense.

Explosion and Fire Hazards

Explosion and fire hazards are grouped together because they both arise from the handling of flammable liquids. Many of the precautions to combat the explosion hazard are similar to those used against the toxic hazard and in consequence these will be dealt with first. The main differences between toxic hazards and explosive hazards arise from the fact that toxicity is a hazard to personnel only, whereas explosions can damage plant as well. Also explosions in confined spaces can do more damage than those in the open, and explosions can lead to fire.

As with toxic hazards, when there is a possibility of fire or explosion it is desirable to ensure that vapours are not allowed to escape in quantity. With toxic hazards the important criterion is the M.A.C. figure. With explosive hazards the criterion is the Lower Explosive Limit. Fortunately, Lower Explosive Limit concentrations are usually a few per cent expressed in volume ratios and not parts per million as for toxic hazards. Unfortunately, many flammable liquids are volatile and give explosive mixtures in equilibrium with the liquid at relatively low temperatures. The temperature at which explosive mixtures are in equilibrium with the liquid under specified conditions is known as the " flash point " of the material. Two common conditions specified lead to the terms " Closed Cup Flash Point " and " Open Cup Flash Point ", the latter being a higher temperature than the former. These properties will be referred to frequently in the next few paragraphs.

The fact that an explosion in a confined space causes more damage than one in the open leads to the recommendation that storage of flammable materials should be outdoors. The relatively high concentration associated with the Lower Explosive Limit reduces the degree of ventilation required to dilute escapes to safe limits compared with toxic materials. In consequence natural air movements can be used except in a few cases where leakage is likely to be heavy.

It must be remembered that, in tanks containing liquids above their closed cup flash point, the vapour space will contain an explosive mixture unless precautions are taken. Floating roof tanks or blanketing with an inert gas may be used to overcome this. Some people argue that explosions are not likely to take place in enclosed vessels because no source of ignition is present. Sources of ignition may arise from many apparently innocent conditions and static electricity has been shown to be capable of causing an explosion.[7] Mention should be made here of the use of flameproofed electrical equipment to B.S.229[8] and of intrinsically safe electrical equipment to B.S.1259.[9] In both cases, certificates that the equipment has passed the appropriate tests at Buxton and Sheffield respectively should be insisted upon. The difference

between the groups of B.S.229 and the classes of B.S.1259 is worth noting. There should be no need to mention that naked flames should be kept out of explosive hazard areas, but the fact that some aluminium paints on rusty steel surfaces can cause sparks under certain conditions is often overlooked. The difficulty of defining the types of aluminium paint which are safe under all conditions has led to the banning of all aluminium paints on steel surfaces by at least one company.

When designing storage installations for flammable liquids it is essential to review the properties of the liquid and to determine which of the government regulations are relevant. Certain materials with a closed cup flash point below 73°F are covered by the Petroleum (Consolidation) Act 1929[10] and by the Petroleum (Mixtures) Order 1929.[11] Typical materials are crude petroleum, gasoline, benzene, heptane, hexane, octane, naphtha, and toluene. Storage of these materials requires a licence and in order to obtain a licence the installation must conform to the requirements of the local authority which normally bases its regulations on the Petroleum-Spirit Model Code.[12] This code gives details of the distance of tanks from boundary fences and from buildings, and the spacing of tanks relative to each other. The precautions to be taken with regard to sources of ignition such as electrical apparatus, static electricity, carrying of matches, boiler houses, and locomotives are listed. Some regulation relating to the design of the tanks (such as minimum plate thickness for above-ground and underground tanks) together with the requirements for tank fittings are given. Figures given in the Act are not quoted in this paper because it is felt to be dangerous to extract them from their context. If difficulty is experienced in obtaining copies of the Model Code similar information is available in Watts.[13]

Many flammable materials with flash points above 73°F are used in industry. Some guidance as to the precautions to be taken with these can be obtained from the Institute of Petroleum Safety Codes,[14] Parts I, II and III. In this code inflammable materials are grouped into

Class A—flash points below 73°F

Class B—flash points between 73°F and 150°F inclusive

Class C—flash points above 150°F.

Class A materials line up with those covered by the Petroleum (Consolidation) Act 1929 but further information is given in the code on the spacing of tanks and on the method of bunding tanks to prevent spread of fire.

Class B liquids are accepted as less hazardous than Class A liquids but, for refinery use, the recommendation is given that tanks for Class B liquids should be treated similarly to those for Class A in order to provide flexibility. Where Class C materials are concerned the fire risk is regarded as being quite small and no restrictions are placed upon the spacing of tanks and bunding is not recommended except where oil might escape and cause damage to a third party. Many people regard this last point, together with the recovery of large spillages, sufficient justification to include bund walls on installations for Class C materials.

The Institute of Petroleum Safety Codes are intended for application to refineries where the quantities handled are very large. In the chemical industry, where the quantities are often smaller, it is difficult to assess whether the recommendations of the I.P. Code should be applied or not. Here the I.C.I. Engineering Codes and Regulations,[15] available from the Royal Society for the Prevention of Accidents, may be useful. At the opposite end of the scale to the Institute of Petroleum Safety Codes is B.S.799 for oil-burning equipment.[16] This gives recommendations for the storage and piping of fuel oil with flash points above 150°F. B.S.2654 entitled *Vertical Mild Steel Storage Tanks, with Butt Welded Shells for the Petroleum Industry* is worthy of mention.[17]

Turning to some specific points not covered by these references; the specific gravity of the vapour can affect the precautions which should be taken. Where the vapour is heavier than air and has an asphixiant or anaesthetic property bund walls should be kept low to reduce the risk to operators. The use of pipe trenches and ducts are not recommended where heavier-than-air vapours are concerned, as these can cause the spread of explosive vapours and fire unless fire stops are incorporated. Above-ground piping makes the dispersion of vapours easier and thus reduces the risk of explosion. Lighter-than-air vapours are not common but where they do occur the use of large areas of solid staging should be avoided. This is especially so where the staging includes deep beams which can help to form pockets of explosive gas.

The need for flame traps on vents carrying flammable vapours is emphasised in many of the references quoted. In this paper only one specific point is made. When installing flame traps on tanks it is common practice to turn the end of the vent pipe over in a swan neck to prevent rain entering the vent. If this is done it is desirable to ensure that, should the vent be ignited, the flame produced does not impinge upon the tank, especially if the tank contains material with a low boiling point. The Texas oil fire gives a lesson on this point.[18] Tanks containing low-boiling-point liquids or liquefied gases should be fitted with water sprays to provide cooling in the event of a fire in the vicinity.

Static electricity has already been mentioned as a possible source of ignition. Most flammable materials are good insulators and in consequence are liable to generate static, especially if small concentrations of impurities are present. It is essential, therefore, to ensure that all equipment is satisfactorily earthed and all piping-flanges bonded for electrical continuity.

The specific comments given are somewhat haphazard but this has been caused by an attempt to refrain from quoting the various references at length.

Corrosion

The fact that a liquid is corrosive may not be regarded as being a hazard in itself. However, if it is combined with toxic, explosive, or other properties it may accentuate the hazard from that source. The first consideration should be to decide on the correct material of construction for the liquids to be handled, taking into account the economic life of the equipment. When dealing with hazardous liquids, safety in handling must not be forgotten but the introduction of this factor into economic equations is difficult. Generalised advice on this is impossible and only experience with a specific fluid and appropriate materials of construction can provide the answer. Laboratory tests on possible materials of construction may provide useful experience but care must be taken that all factors arising in the full scale design are taken into account during the tests. Variations in fluid composition, effects of impingement and velocity, galvanic action, etc., may all enter into the corrosive properties of a liquid. Plant trials are the only completely satisfactory answer but here, failure of equipment will introduce a plant hazard.

Having decided upon the material of construction, it is often necessary for the designer to incorporate a corrosion allowance over and above the design thickness for the equipment. This in itself is not sufficient unless inspection at

intervals is undertaken to ensure that the corrosion allowance has not been consumed. Inspection of vessels and equipment handling toxic materials can be expensive if it is not to introduce a hazard in itself. This should be taken into account when working out the economies of materials of construction.

Manhole covers on tanks requiring inspection should be larger than normal where toxic materials are concerned, to allow for passage of men wearing protective clothing. A suggested minimum is 20 in. diameter. Where the height of the manhole branch exceeds 24 in. the diameter of the manhole should be greater and a suggested minimum is 24 in. It should be emphasised that these minima are based purely on the grounds of safety. Other limitations are imposed by purely mechanical considerations, *e.g.* B.S.1500.[19]

General

When designing pipework to carry hazardous fluids of any sort it is essential to make it robust. Small bore piping should be avoided unless it is very well supported. Small bore connections on vessels should not be used unless adequately reinforced by stiffening ribs. A minimum size of 2 in. is recommended for such connections where practicable. Flanged piping is preferable to screwed fittings and welded pipe is even better in most cases.

Vessels to be installed out of doors which are unlagged should be constructed of steel with good impact strength at low temperatures. This is especially true if the vessel is subject to pressure. It is even more true if its contents have been chilled before entering the tank, but in this case it is less likely to be forgotten.

In the text, references have been given to a number of regulations and codes. Other references of a very general nature include the International Labour Office Model Code.[20] When considering this document care must be taken that local requirements imposed by statute or bye-laws are not more stringent. A second work of a general nature is the publication of the Association of British Chemical Manufacturers entitled *Safety Rules for Use in Chemical Works*,[21] and a third is the National Fire Codes.[22]

Conclusions

The design of storage, pumping and piping installations for handling hazardous liquids is a complex subject. In a paper of this length it is impossible to cover all points in detail but it is hoped that some of the general points raised may be helpful.

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Appendices

Appendix 1 and Appendix 2 appear overleaf on p. 106.

Appendix 1

Toxic hazards

Of the materials listed in the paper, the following are regarded as toxic and the maximum allowable concentrations are given.

Lead	0·15 mg/m³
Mercury	0·10 mg/m³
Chlorine[a]	1·0 p.p.m.
Bromine[a]	0·5 p.p.m.
Ethyl chloride	1000 p.p.m.
Ethylene dichloride[b]	10 p.p.m.
Ethylene dibromide[b]	2 p.p.m.
Tetra-ethyl lead	0·075 mg/m³

[a] These are irritant gases and at concentrations slightly above the M.A.C. values become intolerably irritant subjectively.

[b] Toxic and anaesthetic. Contact with skin or eyes can cause superficial damage such as dermatitis and inflammation.

Appendix 2

Explosion hazards

Of the materials listed in the paper the following are regarded as flammable.

	Ethyl chloride	*Ethylene dichloride*
Vapour density relative to air	2·22	3·42
Vapour pressure at 20°C	1003 mm Hg	64·2 mm Hg
Boiling point	12·2°C (54°F)	83·5°C (182·3°F)
Lower explosion limit	3·8% v/v	5·7% v/v
Upper explosion limit	15·4% v/v	16% v/v
Closed cup flash point	−50°C (−58°F)	10°C (50°F)
Flameproof group (B.S.229)	II	II
Intrinsic safety class (B.S.1259)	Pentane	Pentane

THE MANUFACTURE OF A HIGHLY TOXIC ORGANIC PHOSPHORUS COMPOUND

By J. O. S. McDONALD, B.Sc., A.R.I.C., M.I.Chem.E.*

SUMMARY

This paper describes how a plant designed for the manufacture of an organic phosphorus compound of comparatively low toxicity was modified to permit the safe manufacture of another far more toxic material.

Introduction

Both compounds made by the plant were the major ingredients of systemic pesticides for the protection of crops from aphids and red spider. A systemic insecticide is one with the property of being taken up into the system of the plant treated with it ; the insecticide is transferred to the various parts of the plant so that insects which suck the sap perish.

Field trials carried out upon the second more poisonous compound, *bis* - dimethylamino - fluoro - phosphine oxide, proved its exceptional effectiveness as an insecticide and since an economic process for its manufacture had been developed[1] and a ready sale of the product was assured, there was ample incentive for its early manufacture. Moreover, the plant erected earlier for the small-scale manufacture of the less toxic material required little alteration, from processing considerations, to render it suitable for making the fluoro-phosphine oxide (which for convenience we shall refer hereafter to as compound ' B ').

The Process

The process has been described in detail elsewhere.[1] It consists of three main stages, the preparation of *bis*-dimethylamino-chloro-phosphine oxide, the reaction of this material with potassium fluoride to form ' B ', and the recovery of dimethylamine from dimethylamine hydrochloride formed in the first of these reactions—an operation essential to the economy of the process.

In the first reaction in the series to a solution of phosphorus oxychloride in toluene is added continuously a solution of dimethylamine also in toluene. The following reaction takes place :—

$$3(CH_3)_2NH + POCl_3 = (CH_3)_4N_2POCl + (CH_3)_2NH.HCl$$

The dimethylamine hydrochloride is insoluble and is separated by filtration from the intermediate product, *bis*-dimethylamino-chloro-phosphine oxide, which in the remainder of this paper we shall refer to as compound ' A '. The filtered dimethylamine hydrochloride is dissolved in water and fed continuously to a concentrated solution of caustic soda. This liberates the dimethylamine which is then absorbed in toluene in readiness for the first reaction of the process. The solution of ' A ' is reacted with potassium fluoride according to the following reaction :—

$$(CH_3)_4N_2POCl + KF = (CH_3)_4N_2POF + KCl$$

This reaction requires the presence of a small quantity of water. When the reaction is complete the solution of ' B ' has to be separated from the remaining reaction products which are present in the lower, aqueous layer, as a finely divided slurry. This done the solution is distilled to give a concentrated product ready for formulating into the finished insecticidal preparation, and toluene, which is re-used in the process.

The Hazards

A two-fold hazard really accompanies this process for in addition to the highly toxic ' B ', there is a fire hazard through the use of toluene and dimethylamine. This hazard had been looked after satisfactorily in the original plant. Some of the measures taken included the location of feed-pipes to reactors so as to avoid a free fall of flammable liquids, reactors and piping systems were electrically grounded, flame-proof equipment was employed, and so on.

The action of compound ' B ' upon human beings is to paralyse the central nervous system. If the exposure or dose is large enough complete paralysis and even death can occur. The effect of ' B ' is to reduce the enzyme cholinesterase thereby inhibiting muscular contraction of an affected person. It can be dangerous by contact with the liquid and by inhalation of its vapours.

As to the contact danger, an unpleasant property of ' B ' is the rapidity with which it is absorbed through the skin ; the absorption of 500 mg would be sufficient to cause death, and the absorption of 200 mg would lead to paralysis. With regard to the danger of inhaling vapours of ' B ', it is known that brief exposure to an atmosphere containing $7–13{\cdot}7 \times 10^{-5}$ lb/ft^3 can prove fatal. A concentration of $6{\cdot}2 \times 10^{-8}$ lb/ft^3 or greater can lead to a rapid decline in cholinesterase indicative of a dangerous situation, and atmospheres containing $6{\cdot}2 \times 10^{-9}$ lb/ft^3 or more can cause a steady reduction of the enzyme ; only when its concentration is less than this level can an atmosphere be considered safe to breathe.

These levels of course, do not represent sharp lines of demarcation as between one degree of hazard and another, and the resistance of individuals to anticholinesterase must also vary. But figures did tell us quite clearly the conditions to avoid in order to make the plant safe for the manufacture of ' B '.

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Vapour pressure data

Some of the available data on the vapour pressure of ' B ' and its solutions are given below :—

Vapour pressure of ' B ' in the range 10–50°C is given by:[2]

$$\log p = 8{\cdot}009 - 2522/T$$

Partial pressure of ' B ' in a 10% w/w solution of toluene is given by :

$$\log p = 5{\cdot}88 - 2012/T$$

in a 15% w/w solution the partial pressure of ' B ' is given by :

$$\log p = 6{\cdot}05 - 2012/T$$

Partial pressures of a 5% w/w aqueous solution are given by :

$$\log p = 13{\cdot}61 - \frac{4700}{T}$$

In the above expressions p is the vapour pressure (in mm Hg) and T is the temperature (°C).

From the expression for the pure toxicant, it can be shown that an atmosphere saturated with ' B ' at 25°C would contain a fatal concentration of toxicant.

Elimination and Reduction of Hazards

The above data were useful for investigating the inhalatory dangers likely to arise at various parts of the plant. The original design is shown in Fig. 1 ; this was a plant out in the open. This was considered to be of some advantage since the prevailing winds could assist in dispersing emissions of noxious fumes. Other circumstances conducive to safety were the small area occupied by the plant and the small output of product. The first task was to examine each part of the plant and its every operation for emission or leakage of toxicant.

So far as the two main reactions stages were concerned there was no possibility of rendering them continuous and on that account less hazardous to operate.

A number of more or less obvious practices were adopted in order to remove the various sources of danger. To avoid contact hazards, the plant had to be absolutely free of liquid leaks. Pumps or valves with glands could not be used : pipelines carrying ' B ' or its solutions had a minimum of joints. Where joints could not be avoided they were of the heavy-flanged type with narrow-faced joints. The pipelines were arranged to drain completely once the transference of liquids through them was complete.

Where gravity flow could not be used, transference from one vessel to another was carried out by first partially evacuating the receiving vessel and then opening the line connecting the two vessels. Pumps were used only for the transference of harmless fluids such as fresh or distilled toluene.

Protective clothing of non-absorbent, water-proof material was worn by the plant operators ; this clothing was washed down in warm water before being removed by an operator so that when he returned to his job it would be in clean, uncontaminated clothing.

Making the main reaction safe

Clearly one of the main sources of hazard in the entire process would be where the reaction producing ' B ' was carried

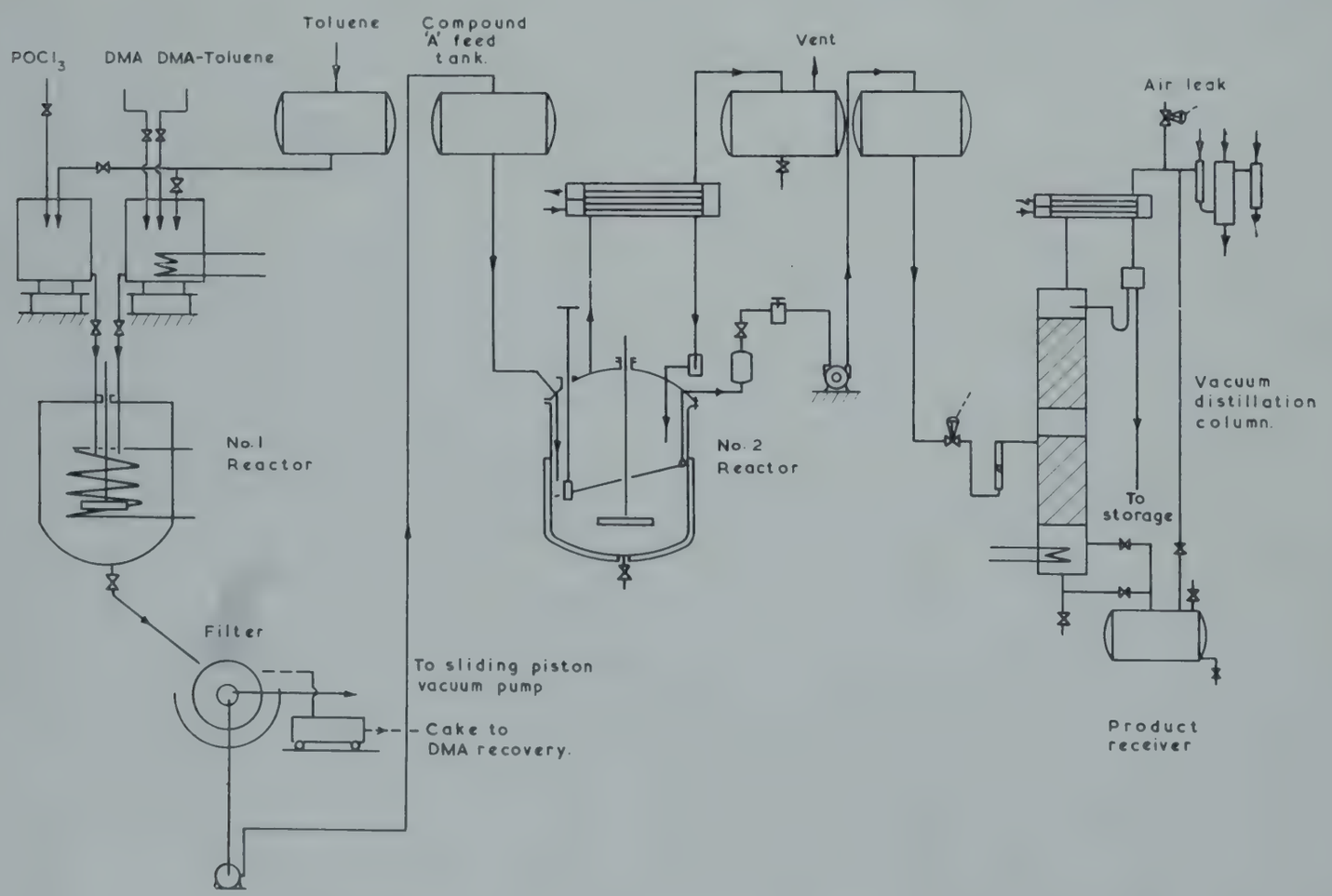

Fig. 1.—*Plant before modification*

out. The main features of the reaction vessel as originally available are shown in Fig. 2. Its purpose had been to react together solid potassium hydroxide with a solution of ' A ' in toluene, the product being considerably less toxic than ' B '. After the reaction the products were cooled and allowed to settle. The clear solution would then be transferred to storage by means of the rotary pump and the dip-pipe.

In the modified arrangements at this reactor the pump was discarded. The dip-pipe was operated manually by means of a stainless steel rod which passed through a stuffing box on the cover of the vessel. The exposed end of the rod was clearly a source of contact hazard, despite any wiping action of the packing, and it was therefore totally enclosed in an elongated leather bellows. At the same time it was arranged that the rod could be operated remotely by means of a small compressed-air hoist.

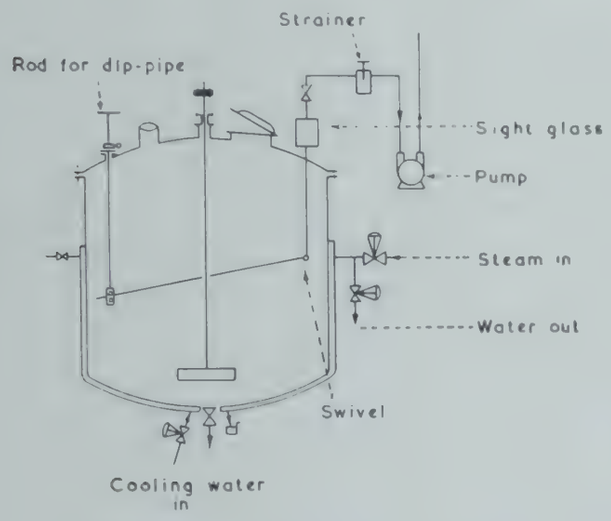

Fig. 2.—*Reaction vessel as originally available*

The dip-pipe was connected to a packed swivel fitted inside the vessel. The swivel was removed altogether and replaced by a short piece of flexible stainless steel hose, the open end of which was positioned by the rod. The dip-pipe connection on the vessel was connected through a sightglass of enlarged section to a tank of somewhat greater capacity than that of the vessel. In order to transfer the contents of the reactor, the receiver tank would be partially evacuated. After this operation the solution of ' B ' would be run by gravity to one of two storage tanks, in readiness for distillation.

Another possible source of contact hazard was the gland of the agitator shaft ; it was possible for toxicant solution to creep past the packing on to the exposed length of shaft near the motor gear unit coupling. To reduce this danger the lantern ring of the gland was put under a positive pressure of several feet of water.

The arrangements which were adopted at the main reaction stage to eliminate the contact hazards are summarised in Fig. 3.

Inhalatory risks at the main reaction stage

From the vessel in its original form hazards through inhaling vapours of the compound ' B ' could arise from at least three causes, the emission in each case being through the vent of the reflux condenser. These were :—

(*a*) displacement of the vessel atmosphere during the charging of reactants ;

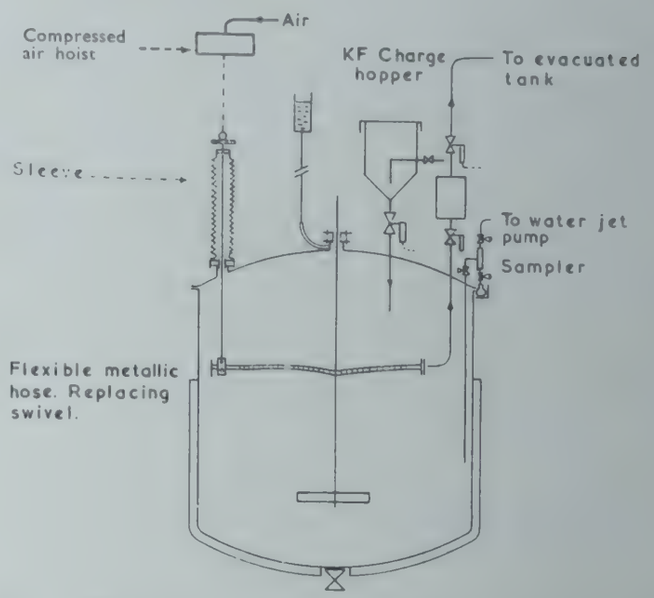

Fig. 3.—*Arrangements of main reaction stage to eliminate contact hazards*

(*b*) expansion of the vessel atmosphere in heating the contents from the ambient temperature to the reaction temperature of 90–95°C ;

(*c*) carryover with non-condensible gases liberated during the course of the reaction.

To estimate the amount of ' B ' through the first of these mechanisms it was assumed that the condenser, which was not designed as a cooler-condenser, would cool the outgoing gases to 30°C, but not below this temperature. It was also assumed that the atmospheres discharged from the vessel were saturated with respect to ' B '. The estimated amounts discharged through the condenser through causes (*a*) and (*b*) were 0·0025 and 0·0033 lb, or a total in round figures of 0·006 lb. This would be discharged within 10–15 minutes.

Mechanism (*c*) did not appear to enter the picture although as shown below, provision was made for dealing with its possible occurrence.

The quantity of 0·006 lb is capable of rendering 60 ft³ air lethal. For absolute safety it would have to be dispersed through a volume of 900 000 ft³. Clearly there were serious inhalatory risks at the main reactor and they were reduced to a safe level by the means shown in Fig. 4. A condenser with

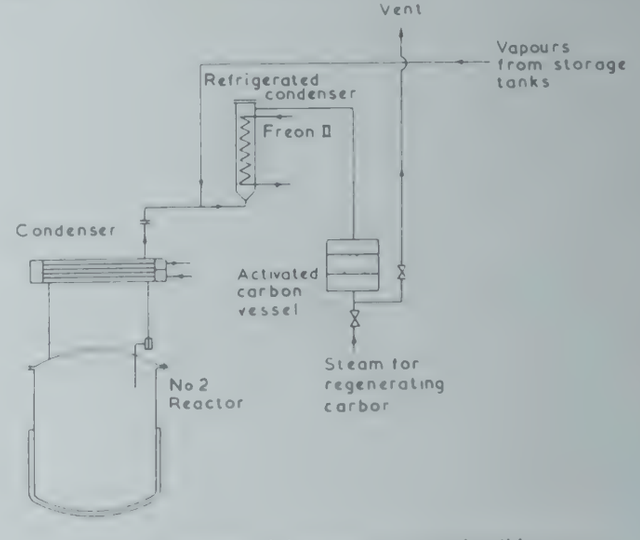

Fig. 4.—*Recovery of dangerous non-condensible gases*

Freon 12 evaporating inside the coils was fitted downstream of the reflux condenser and beyond this a shallow bed of activated carbon was installed to remove the last traces of ' B ' and toluene. The additional vessels were arranged to allow safe regeneration of the carbon. Thus the steam-plus-solvent and toxicant would condense in the refrigerated condenser and flow from it by gravity back into the reactor.

A final point about the reactor is the method of adding the solid reactant, potassium fluoride. In the process previously carried out in this vessel the charge of solid caustic potash was introduced into the vessel through a quick-opening lid on the cover. This practice could not be contemplated in the case of compound ' B '. Instead a 4-inch connection was welded to the cover of the vessel, and to this was attached a compressed-air operated lubricated plug-cock. Above this valve was fitted a small hopper just sufficient to carry the charge of fluoride necessary for a single reaction. At one time the use of a double-valve feed hopper had been contemplated but the idea was abandoned as being too complicated. The charge was added with the valve closed—indeed the lid of the hopper could only be lifted when the valve was in this position. Once the operator had retired to a safe distance the discharge valve would be opened and the charge of fluoride emptied into the vessel. It was possible to sluice the hopper with a small quantity of water after each charge.

Other methods of making this addition were tested ; one suggestion was to fluidise the fluoride and to pump it by means of a positive displacement screw pump directly into the vessel. Although a number of finely divided solids have been pumped successfully by this method potassium fluoride has not prove to be one of them and the idea was discarded. Another method was to convey the charge as a slurry in toluene to the reactor, but this too proved unpractical.

Hazards at storage tanks

The filling and breathing of storage tanks containing solutions of ' B ' also constituted a hazard. A 500-gallon storage tank containing a small quantity of 15% solution of ' B ' in undergoing a rise of temperature from 10–25°C would discharge about 0·000 56 lb of ' B ' to atmosphere. This small quantity would be sufficient to produce a fatal level of concentration in a volume of 9 ft³ and for complete safety would have to be dispersed in a volume of some 90 000 ft³. However, this quantity is evolved over a comparatively long period.

When the filling emissions are considered the figures are much more serious ; if the tank and contents are initially at 10°C then about 0·0039 lb of toxicant is emitted. This is sufficient to render lethal a volume of 50 ft³ and for safety would have to be dispersed in a volume of over 600 000 ft³. If the temperature of tank and contents were 25°C the situation would be even worse since the quantity discharged would be about 0·008 lb and this would render lethal a volume of 112 ft³ and for safety would have to be evenly distributed through a volume of over a million cubic feet.

The emissions were dealt with by connecting the tank vents to a point between the reflux condenser and the refrigerated condenser shown in Fig. 4.

Treatment of solvent

After it is distilled from the main pocket, toluene is returned to the process for further use. It is for example mixed with phosphorus oxychloride to provide one of the reactants for No. 1 reaction. It is used also for the absorption of recovered DMA and for washing the cake of DMA hydrochloride arising from the first reaction.

The safety of No. 1 reaction and its preparatory operations, the filtration following it, and the recovery of DMA depends therefore to some extent upon the use of a solvent substantially uncontaminated by ' B '.

The distillation column available was found to be capable of reducing the level of contamination to somewhere in the range 15–200 p.p.m. This was not considered to be low enough since something like 0·2 p.p.m. was required for

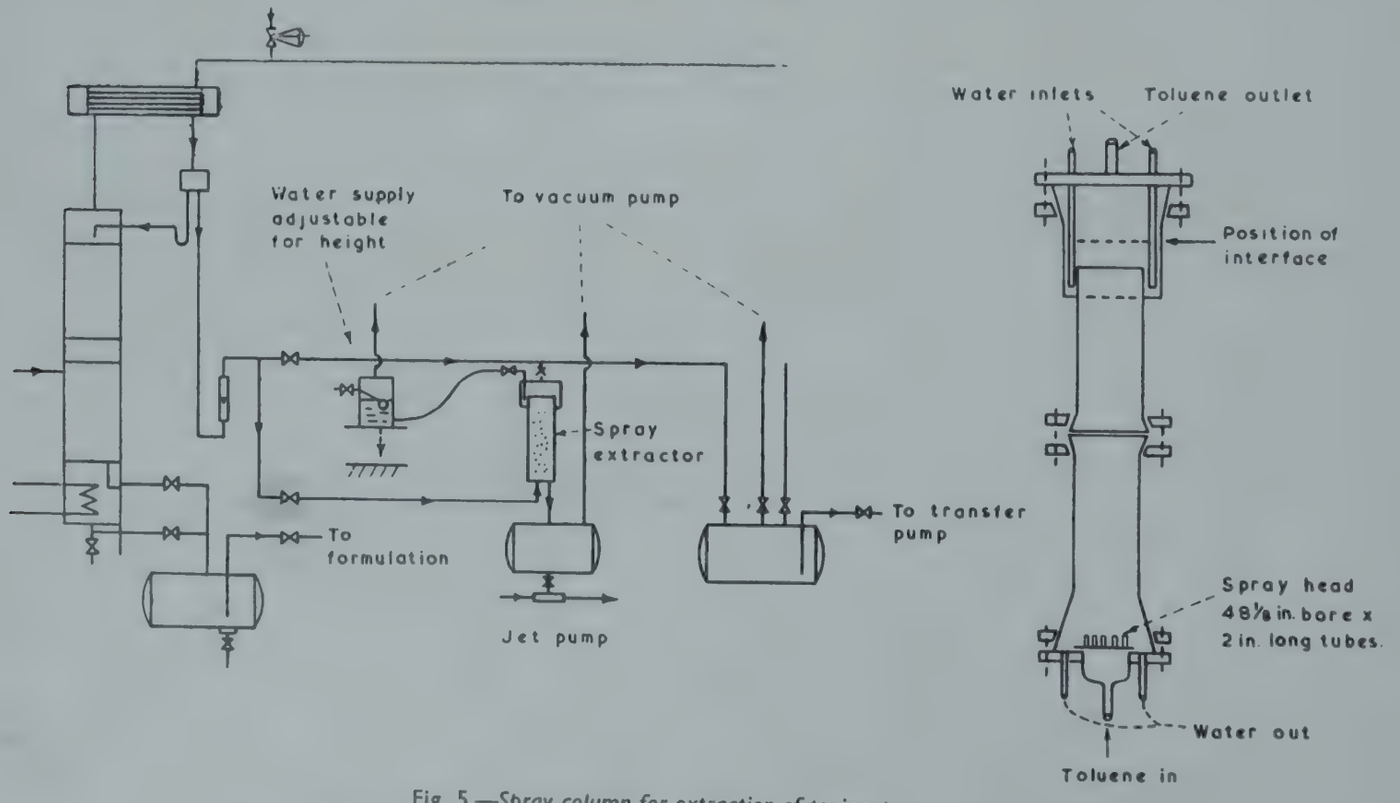

Fig. 5.—*Spray column for extraction of toxicant*

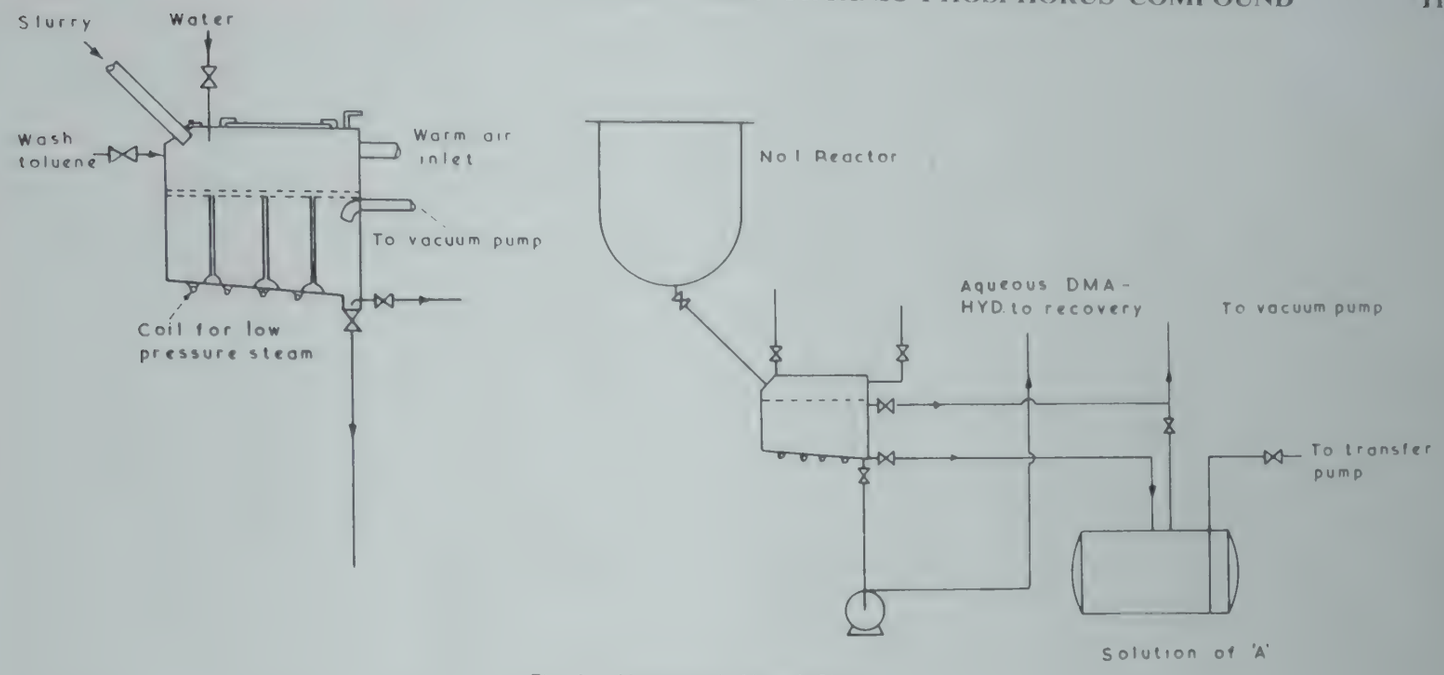

Fig. 6.—*Home-made Nutsch filter*

reasonable safety. It seemed doubtful whether this level of purity could be obtained by distillation.

The column, which was designed to operate at a vacuum of 28½ in. Hg, was provided with a water-ring vacuum pump in place of a two-stage ejector set used previously. The substitution was made because uncontrollable fluctuations in steam supply to the ejectors had previously led to upsets in operating vacuum. While this change was conducive to more stable operation for the production of purer toluene another measure was necessary.

This consisted of making use of the greater solubility of ' B ' in water compared with toluene ; thus the toxicant was extracted with water from toluene, by means of a small spray column fitted between the distillation column and the toluene collecting tanks. In this unit (Fig. 5) toluene is bubbled through the extracting water which passes downwards through the apparatus. The extractor was designed to reduce the ' B ' content of 30 gal/h of toluene from 200 p.p.m. to 0·2 p.p.m. A greater extracting effect could have been obtained, if required, by interposing another cylindrical section between the main joint.

Although the provision of a very pure toluene was an important contribution to the safety of the earlier stages of the process additional measures were taken to improve safety. Thus the pumps used for the transference or circulation of toluene were arranged to have their glands under suction when in operation. A further measure was the filter for the hydrochloride. This piece of equipment replaced a small rotary vacuum filter which was not mechanically reliable enough to be a safe means of filtration. The replacement was a home-made Nutsch filter (Fig. 6). Contact with the cake could be avoided by dissolving it, after washing, in water and by pumping the aqueous hydrochloride solution to the recovery process. The filter cloth after this operation can be dried by drawing warm air through the filter. The design still allowed for the manual removal of cake, but the dissolution method was much the safer since it eliminated contact with the cake.

Transfer of toxicant and its solutions

As indicated earlier in this paper, compound ' B ' or its solutions were not transferred by pumping direct but by evacuating the receiving vessels. The pumps used for evacuation were of the water-ring type and they were particularly suitable for this purpose because their service water supply served to condense to toxicant vapours. The air-discharge pipes from the pumps were taken to a height to ensure that any uncondensed toxicant would be carried away beyond the operating area. The water discharged from the pumps passed through beds of activated carbon to remove the traces of dissolved toxicant.

For filling containers at the final stage of the process, glove boxes fitted with quick opening air locks were employed. The amount fed to a container was controlled by means of a conductance electrode system which worked in conjunction with a solenoid valve.

In addition to the steps described other safeguards were provided. For emergencies, respiratory apparatus was available, the air being supplied from a small diaphragm compressor with its intake situated well clear of the plant area. In order to provide a ready source of decontamination in the event of a spillage of ' B ' or its solutions, a header tank containing a supply of hypochlorite solution was also installed. A highly desirable feature at this plant would have been a system of monitoring continuously the condition of the atmosphere at various danger points. Unfortunately no such equipment appeared to be available at the time of making the modifications described, and reliance had to be placed upon frequent manual sampling and chemical analysis for this purpose.

Finally the operating and maintenance staff were given frequent and regular medical examinations to ensure that their cholinesterase levels had not suffered through their presence on the plant.

The foregoing were some of the main steps which were taken to make an existing plant safe for the manufacture of a useful but extremely dangerous chemical.

References

1 Pianka, M. and The Murphy Chemical Co. Ltd. *British Patent* 742 699.

2 Schrader, G. "*Die Entwicklung Neuer Insectide auf der Base der Fluor und Phosphor Verbindungen.*"

The manuscript of this paper was received on 15 *March*, 1960.

DISCUSSION OF PAPERS AT THE FOURTH SESSION

Mr. E. WARDE stated that there were many items of equipment fabricated from Monel metal in use in the chemical and allied industries, the majority of which had given exceptional service and had been produced, in most cases, by the fusion-welding of plates, sheets, bars, tubes, etc. The most severe radiographic standard which had been demanded up to the time at which the Springfields project was conceived, was that of the then current version of the A.S.M.E. Boiler and Pressure Vessel Code. The various electrodes and the filler-wire discussed by the authors were covered by the relevant A.S.T.M./A.W.S. Specifications. The appendix to the electrode and filler specification suggested that if radiography were required, it should be in accordance with the A.S.M.E. Boiler and Pressure Vessel Code, Section VIII latest edition, Paragraph UW-51. Radiography of weld deposits was not mandatory for acceptance of electrodes and fillers. It was a remarkable tribute to the British chemical plant industry that it had achieved a radiographic standard in excess of Lloyd's Class 1, using electrodes and fillers primarily developed to meet only A.S.T.M./A.W.S. Specifications.

Regarding the welding of nickel-base alloys, Mr. Warde considered that the documentation was sufficient to enable the British chemical plant industry to fabricate equipment in those materials in accordance with the requirements of the A.S.M.E. Code. Such fabrications were regularly carried out in various shops in the U.K.

Monel metal had a long record of service with hydrofluoric acid, particularly in the petroleum and the petro-chemical industries. The production of high-octane gasolines for aviation was associated, to a very great degree, with the Phillips alkylation process using hydrofluoric acid as a catalyst. Usually the acid was regenerated by distillation, to recover both anhydrous and azeotropic (nominal 40%) acid as top and bottom products respectively : hence the use of Monel for the distillation column and ancillary equipment. One such unit, producing detergent alkylate, had been in service in the U.K. for over five trouble-free years. Literature references go back as early as 1943 detailing actual plant experiences which did not follow those of the present authors.

Most of the references emphasised the importance of avoiding oxidising conditions, for example, with dissolved air or an inorganic radical such as ferric or nitrate ion. The technical publications of the speaker's company made similar emphasis and there were case histories on file of the premature failure of Monel and other nickel-base alloys operating under acidic oxidising conditions. The N.A.C.E. Technical Committee Report publication 59–14 was pertinent in that connection.

The presence of even traces of impurities could have a most exceptional effect and it was the speaker's opinion that the influence of sulphides was similar, and even greater than that of nitrates. Furthermore both, in combination, exerted an even greater corrosive influence than either species individually. That comment was specific to the writer's own work on Monel and hydrofluoric acid. A similar case involving an 18/8 Ti vessel handling traces of sulphides in an acid fluoride environment has been reported from Springfields and in that case both parent and weld metal suffered accelerated attack. Excessive corrosion might well be associated with impurities introduced by the material being processed at Springfields. Mr. Warde emphasised that his company was actively engaged, in close collaboration with the Culcheth Laboratories of U.K.A.E.A., on the general problem of excessive attack on both weld and parent Monel metal under conditions similar to those at Springfields.

The problem of the apparent " galvanic " variation of the weld deposits was most complex and reports from the United States of America indicated that while excessive corrosion of parent Monel metal had been experienced, problems had not been encountered with weld deposits. The plant in question was handling materials similar to those at Springfields.

Mr. Warde continued that it would be of interest to know :

If the welds were radiographed prior to test and, if so, what standards were achieved?

Were tests, carried out in a media with 1% oxygen in the atmosphere, expected to provide a valid indication of plant behaviour under the more rigorous conditions of oxygen control currently practised?

In describing the relative corrosion of welds, the terms " anodic " and " cathodic " were used. Had potential measurements actually been made on 140, 130, and 60 weld metal-deposits and parent metal under conditions which simulated those associated with plant operation? As the cause of the accelerated weld corrosion was still a matter of conjecture, would it not be prudent to suspend judgment until the matter had been investigated more exhaustively?

Mr. HILL said that the welds on the specimens shown had been radiographed and passed to the standards described. Further tests, not described in the paper, had been carried out on specimens having repeat welds, *i.e.* the weld had been cut out and remade a number of times. That had been done because the joints in the plant which had been re-welded in order to establish the necessary weld standard appeared to corrode faster than joints made correctly on the first try.

The test specimens agreed qualitatively with the plant findings, but it was still too early to state rates.

With regard to oxygen contents of the atmospheres, he agreed that 1% was very high. All it probably indicated was that the solution was saturated with oxygen. That could be achieved at figures fairly close to 0·1%. It had been found that tests of such nature, where oxygen was passed through the atmosphere at a properly controlled rate, could be related to plant performance.

The use of the term " cathodic " was made on the assumption that electrolytic corrosion was involved. He meant to imply that the welded metal was not corroding as fast as the parent metal. He agreed that it was assuming a lot to say the weld was cathodic.

It was intended to make measurements of the potential across the welds, but they were very difficult to do in a way which would yield results of value.

Mr. Warde had commented on the fact that the weld specifications demanded for the Springfields plant were higher than the then currently accepted codes. A similar situation had previously arisen at Windscale with regard to stainless steel welding. The necessity for such strict welding specifications should be understood.

In many processes the change from mild steel to stainless steel or some other alloy frequently resulted in a change from corrosive to virtually non-corrosive conditions, and all that was required of welding, apart from considerations of strength, was that it should plug the gap. But when dealing with a medium that corroded the corrosion-resistant alloy and where the corrosion allowance was significant in terms of plant life, then porosity in welds and similar faults assumed added importance apart from structural soundness. If there were an air bubble in the middle of the weld it reduced the thickness which the acid had to penetrate.

He supported Mr. Warde completely on the matter of the presence of impurities. If a test were made in pure hydrogen fluoride, one did not get the correct corrosion performance. It was not yet known what the impurities were at the Springfields plant. It had a general relevance insofar as he did not know any chemical processes in existence which did not have impurities associated with them. The contributions of himself and his co-author were given in the hope that people wishing to use hydrogen fluoride would have some idea of the problems.

Mr. J. I. KRZYMUSKI said that MacDonald had described a number of steps taken during the design stage to eliminate the emission of toxic vapours. What warning was given to the operator that the plant was dangerous? The compound could not be smelt so easily as hydrogen fluoride.

Mr. MACDONALD said that the only direct indication of a safe plant would be the absence of cholinesterase depression on the part of the operators. Any leakage of compound 'B' would be shown by an oily appearance and vapours would be detected by the analyst if they persisted. Beyond that, there was little that could be done to detect toxicant 'B'. All joints had to be scrutinised regularly to make certain there was no leakage, alarms were fitted to the condensers on the water supply of the distillation column and the refrigeration vent-condenser. There were only two or three cases of any serious cholinesterase depression and they occurred before the original plant was altered but they had had a month's operation of the unaltered plant under very careful conditions. He believed that the cholinesterase of the person in charge of the plant dropped from 100 to 70 over a period of four weeks, one operator experienced a depression to 30, another to about 40–45; those results were considered to indicate an unsafe plant. The arrangements made were precautionary and they had no means of rapidly detecting the presence of compound 'B'; chemical analyses performed on manual samples taken at frequent intervals took about 3 hours per analysis.

Mr. HILL said that detection gear had been installed at Springfields to detect hydrogen fluoride but the nose was far better. Many cases had occurred where a leak could be seen and smelt, but because the wind did not happen to have blown the vapours near the instrument the alarm had not gone off. The whole room or the whole area had to be scanned for effective detection by instruments.

Mr. D. B. PURCHAS said that while MacDonald was making the obnoxious compound he had been making the same compound elsewhere. It was most interesting to compare in retrospect their respective methods.

There was a marked divergence in basic philosophy. Thus Macdonald had put the entire plant in the open air with the idea that anything escaping by leakage would be able to get right away. In his own company they had first split the process into two independent stages. The first stage produced a non-toxic intermediate, and was therefore treated as a normal industrial process in one of the ordinary factory buildings. The second stage, wherein the highly toxic product was formed, was placed right at the back of the factory site, well away from other operations. It was then subdivided into two connected parts, the first part handling safe materials and the second toxic materials. The toxic section was housed in a locked building, with the safe section for convenience located adjacent to it in the open air. All operation of the toxic section was by remote control, using simple extended spindles, etc., protruding into a control cabin. Fans kept the locked building under a slight vacuum and discharged exit gases high into the atmosphere.

That approach had avoided some of the detailed problems encountered by Macdonald, such as, for example, the need he felt to irrigate the agitator gland on his reaction vessel. Nor did they need to worry about recovering solvent uncontaminated by the toxic product since solvent used in the toxic second stage of the process was never recycled to the safe first stage.

Although they were thus able to discharge any toxic gases well up into the atmosphere, having first diluted them liberally with large amounts of air, there was nonetheless a factor which worried them and which should surely have been of even more concern to Macdonald; that factor was the weather. It is all very well discharging gases into the upper air, but a temperature inversion such as caused fog and mist to linger would also cause stack gases to return to the ground. In Macdonald's case, in addition to that risk, was there not also the danger that the wind, free to blow through the plant in any direction, might have caused very dangerous pockets of gas to build up in quite unpredictable localities?

In connection with that type of hazard, Macdonald had mentioned the use of a refrigerated condenser to minimise the discharge of organic vapours into the air. He had also mentioned non-condensable gases. There appeared to be something a little incompatible about those two points.

The hazards associated with the hopper device for adding potassium fluoride to the reactor were rather frightening. At his company such hazards had been avoided by making that stage of the process a completely liquid reaction between aqueous potassium fluoride and a solution of the intermediate in an organic solvent. The technique had the further advantage that there was no need for a filtration step as used by Macdonald; instead, gravity separation of the aqueous and organic solutions sufficed.

Macdonald referred to the regular checks on cholinesterase level of operating and maintenance staff. The same procedure was used at Mr. Purchas' company, where in no case did the level fall to any serious extent for staff on the plant producing this particularly toxic compound. By contrast, however, an extremely serious incident occurred on a different plant manufacturing another organophosphorus insecticide which had been regarded as relatively safe to handle. Of the three people affected, two recovered fairly quickly, but the third

suffered permanent disability ; at one time seriously paralysed, she has never fully recovered. Did Macdonald have any serious incidents, or was the worst experienced merely a slight fall in cholinesterase level which resulted in the individual affected being switched temporarily to other work?

Mr. MACDONALD said that the experience with the particular 2nd stage reaction, where they added solid potassium fluoride to the solution of ' A ' in toluene, was that it was one requiring the supply of heat ; it was not an exothermic reaction. The reactions were different : why the difference should cause one to be exothermic and the other endothermic was not clear. However, the Schradan reaction was known to get out of hand if an impurity were present in the reactants. If the main reactant products were transferred from the reaction vessel to the intermediate storage tank, in pumping it down in order to do the transference, something like 000·7 lb of ' B ' would be transferred. That would take place four times a day and was not a very serious load for the activated carbon adsorbers. Throughout the plant adsorption was used only for removing traces of toxicant only. On the question of the effectiveness of activated charcoal as an adsorbent for toxicant traces he was reminded of a paper by Sharp.[1]

The treatment of activated carbon and the recovery of the material from it was arranged so that the recovered material flowed back again into the reactor and the toxicants, assuming they were undecomposed by the steaming-out, did not therefore reach the atmosphere but flowed instead into the reaction vessel. With regard to the treatment of material recovered from activated carbon from the water-ring pumps, the idea was to use the recovered liquids to dissolve the caustic soda used in the recovery process.

Thus in the recovery system where the caustic soda was virtually boiling the toxicants would be destroyed chemically.

There was another process that they had worked out for full-scale use but did not use because it was not economic. The idea was to combine the aqueous toxicant solutions from all sources and to use them for making caustic soda solution which would be fed continuously with aqueous dimethylamine hydrochloride to a combined reactor-distillation column. That would yield pure anhydrous dimethylamine as head product and sodium chloride solution as bottoms. The adoption of that modification would have provided a means of destroying the toxicant solutions and at the same time would have eliminated a fire hazard.

Mr. Purchas had over-estimated the difficulties of safely transferring solids to the reactor. In any case the slight disadvantage of handling solid potassium fluoride was more than offset by the very high yields, which closely approached the theoretical, as well as the very easily controlled and therefore safe reaction. There was no possibility of the reaction getting out of hand and rendering hazardous an area for miles around the plant. Despite the fact that the solvent medium had to be recovered the economics of the process certainly did not suffer seriously partly because raw material costs were the principle element of product cost.

It should be mentioned too that the patent position called for a process different from the one to which Mr. Purchas referred.

With regard to Mr. Purchas's comments on the refrigerated condenser, the removal of small quantities of condensable vapours in the presence of non-condensed gases was very widely practised (*e.g.* dehumidification). The calculation might be awkward in the case considered, since there were present three condensables, one of which was immiscible, and in fact a method had to be devised. Checked against small-scale tests it was shown to give an overestimate of the surface required for a given duty. The condenser used—a piece of equipment released from the earlier process—was shown to have a healthy safety-margin of surface and was able to handle the filling displacement even were the vessel reflux condenser to be inoperative. Moreover, the adsorber placed downstream of the refrigerated condenser also had sufficient capacity, when fresh, to handle twice the entire vapour load discharged during the charging operation.

As for design philosophy, the decision to place the plant in the open was taken when it was first designed for comparatively innocuous compound. It was true that the fact that the plant was in the open was looked upon as an advantage in the event of an unexpected leakage of toxicant, but that view did not amount to a design philosophy. In the case of the plant modified to make compound ' B ', at no time was the view taken that toxic vapours could be allowed to escape to the surroundings. On the contrary it was decided to allow only the merest traces to be vented and then only at a height. Part of the paper indeed was concerned to show how little of compound ' B ' could be tolerated.

Dr. J. H. BURGOYNE asked Miller and Penny about the propagation of the acetylene explosion at and around atmospheric pressure. In the study made, a 12 in. pipe was used, and initiation was over the whole area of cross-section of the pipe by means of an explosion at higher pressure bursting a diaphragm. Did the author consider that there was any prospect of the explosion propagating at atmospheric pressure in pipes of smaller diameter? Did they think that shock was essential to initiation at this pressure, or was it sufficient to initiate by flame across the whole area?

Dr. MILLER said that the incidents that occurred in the field were definitely cases of initiation across the whole length of the pipe. That was so in Germany. There were similar cases in America. In an American case, the operating pressure was 15 lb/in^2. The tests done by the Germans, down to slightly sub-atmospheric pressures, were definitely cases of initiation across the whole length of the pipe (which was 20m long and 12 in. diameter). In their own experiments propagation had been made to go along 600 ft of 3 in. pipe. Initiation at a point did tend to die out, certainly at atmospheric pressure and up to about 22 lb/in^2. At high pressures, however, point initiation did set up progressive explosion.

Dr. BURGOYNE asked if the shock was necessary.

Dr. MILLER replied that it was not and it could be done by having a flame round the whole perimeter.

Mr. D. B. PURCHAS took up Macdonald's point about the toxicity of the compounds. On the question of what level of cholinesterase the human body could suffer, one point was to realise that the figures were on a purely arbitrary scale. They did not mean anything in a direct sense. One could exceed a value of 100 ; it was not a percentage level. His company had encountered levels down below 10, which had caused considerable alarm and despondency, but the patients always recovered. How low a level could be tolerated had not been determined, so far as he was aware.

On the question of toxicity and the spraying of cocoa and other products with the compounds, the whole principle on

which they were founded was that systemic insecticides by definition entered the system of the plant. Once in the plant, they hydrolised to form non-toxic decomposition products, and a tremendous amount of work went into it determining the rate at which that breakdown occurred. The particular insecticide had a high rate of breakdown, so the period referred to by Mr. Macdonald was quite safe.

Dr. F. SJENITZER referred to p. 93 of the paper by Miller and Penny. It was rather surprising that it was stated that bursting discs were not successful. Would the authors expound on how they had inserted the bursting discs?

Mr. PENNY said they were not very confident about bursting discs in an explosive system. In actual experimental work, they had set up systems of a long pipe with a T-piece, and at the other end equipment for measuring velocities. They had worked at 10–20 atm, not atmospheric pressure, and the velocity was 2000 m/s. They had put in bursting discs to see what the effect was on the velocity measured : it was nil. Detonation was set up in the pipe at a distance of not more than about 4 ft from the initiating point and travelled at a stable rate, blew out the bursting disc, but carried on completely unaffected.

They had then put in a bursting disc close to the initiation point. Again the bursting disc operated, and they had explosion velocities of the order of 1800 m/s. In other words, a bursting disc simply took no notice of a detonation in the pipeline. Where bursting discs were useful was where the reaction was being carried out in a solvent and it might run away but not actually explode. An acetylene reaction was almost invariably highly exothermic. The running away could develop high pressures at considerable temperatures, fairly rapidly from the ordinary point of view, but very slowly compared with explosion and a bursting disc was then effective in relieving the vessel. Then there was always the problem as to what to do with the vented materials : so far the authors discharged them high up into the atmosphere, where a large flame would not do any harm. When really big plants came into production that provision might be inadequate.

Mr. G. V. DAY said that in view of the difficulty that had been experienced in the use of Monel, he wondered how much attention had been given to the possibility of using various types of plastic material—P.V.C. or non-porous carbons, or ebonite. With moderate temperatures they might be useful. Mention had been made of air-operated valves with Monel bellows. Had the use of diaphragm valves been considered, such as the Saunders type?

Polythene has been used successfully for cold liquid hydrogen fluoride at all strengths chiefly as piping. Rigid P.V.C. has been used successfully in contact with hydrogen fluoride vapour diluted with air, steam and nitrogen, mainly as fume ducts and fume cupboards.

Most of the problems of corrosion by hydrogen fluoride concerned the containment of hydrogen fluoride at temperatures above the safe limit for polythene and P.V.C.

Mr. KNOTT said that they had used P.T.F.E. which was rather difficult to fabricate and handle. It had been used successfully in jointing material and in bellows. It was also used successfully as a lining for pipes but that was rather a new development and they had no experience of it in a practical sense.

The problem of air-operated valves had been attacked in two ways. One was to keep the bellows warm, which had been the practical way of dealing with those already installed. P.T.F.E. bellows were being developed. There were some difficulties in application but once they were overcome the bellows would probably be successful.

Another way of dealing with the problem in one particular instance was to do away with bellows altogether, and to use a stuffing box type of gland packed with nitrogen to prevent escape of hydrogen fluoride.

Mr. J. O. S. MACDONALD asked Grover about putting one liquid on top of another to prevent the evaporation of the liquid underneath. That had occurred twice in the process reported in his own paper. The difficulty was that they could not find a liquid that would float and yet not extract the toxicant. Others which were satisfactory chemically would not float. Had Grover any experience of small plastic beads which had been used as layers on top of the surfaces for restraining evaporation?

Mr. GROVER said that it was often difficult to find a fluid which would float and which was non-volatile. Fortunately, the substances they dealt with were, on the whole, fairly heavy, so that they had quite a wide selection of liquids which would float. Beads would probably have some use.

Mr. A. H. GOODLIFFE said that appreciable portions of the beads sank after a time and caused operational difficulties. Their use was of doubtful value.

Mr. P. M. SALES, referring to the section of the paper by Miller and Penny on explosion arrestors packed with Raschig rings, asked what the diameter of the arrestor tower was. What would be the effect of varying the dimensions of the pipe on the height of packing required to quench detonation? What would be the effect of gas flow on the behaviour of an explosion arrestor? Would it be greatly different from that under the static conditions employed in his tests?

Dr. MILLER said that the Raschig rings were 1 in. diameter in a tower 9 in. diameter. They had not done any field work with a larger diameter pipe, but with a larger diameter pipe a larger diameter tower would be needed to quench an explosion : the height should be much the same as for a smaller pipe. Detonation velocity was only slightly dependent on pipe diameter ; the quenching would be much the same. Tower explosion-arrestors of larger diameter were in use in various parts of the world. Gas velocity did not affect the results very much. Their experimental work was designed originally to have gas flow, but so far they had not been able to carry out tests with gas flow. The authors did not think it would make very much difference, if any.

Mr. P. M. ORTON referred to the statement of Miller and Penny that, in handling compressed acetylene where there was electrical equipment, close contact with any possible source of acetylene escape and a consequent ignition must be avoided. Did he recommend that the electrical equipment be submitted to water gauge air pressure to prevent source of ignition, or was it regarded as adequate to use flame-proof equipment conforming to B.S. 229?

Dr. MILLER replied that there was no flame-proof equipment available to a British Standard. Acetylene and hydrogen were

in Group 4. Recently, some flame-proof equipment for hydrogen had been claimed, but he did not know whether that was fully acceptable. There was no British Standard for flame-proof equipment for use with acetylene. It was possible to avoid ignition by the pressurising of the plant and it had been done on large-scale plant : it worked quite satisfactorily.

Mr. K. M. HILL said that Macdonald had described a very elegant method for purifying the toluene after it had been through the distillation column ; the necessity for that was based on the estimate that it was not possible to get down below 15 p.p.m. in the column. Was that based on vapour pressure data or carry over data?

Mr. MACDONALD replied that it was carry-over data. It was a point very well worth looking at from a more fundamental angle. Their experience with the packed distillation column was that however they manipulated the reflux ratio they could not improve upon those figures. His conclusion was that it was due to entrainment and apart from fine mesh entrainment mats which were installed early on, they could do nothing to improve the purity of the solvent.

Mr. D. F. RILEY said that in the practical design of storage tank installations for flammable liquids it was quite a common practice to put a flame trap of conventional gauze-type over the end of the vent. He had done it many times. He had been fortunate in that none of the tanks he had put in had ever suffered an accident, but he often wondered whether, if there was any fire, those flame traps would, in fact, be of value. Was there any information available which would help one to decide whether they were of any use?

Mr. PALMER said that for petroleum storage, the practice had been to use a 28 mesh gauze, which was 28 meshes to the linear inch, either a single or double layer at the end of the vent pipe. Some tests had been done using propane/air mixture which showed that, if the flame trap was put right at the end and ignition occurred that end, it would cope with the flame and hold it. But if the flow of vapour came up below the flame trap, that flame trap would get very hot very quickly and did not have much margin to spare. If the flame trap was put lower down the pipe in an attempt to protect it from external influences, the speed would be much higher and it would probably fail. The flame trap had to be put within one foot of the open end.

Mr. GROVER said that he was not aware of other research in the field.

Mr. F. FARRINGTON said that Klinkenberg and Van der Minne[2] had recommended limiting pipeline velocities of gasoline to 1 metre per second to avoid the build-up of static ; he asked whether Grover knew of the application of similar limitations to other liquids.

Dr. L. J. BURRAGE wrote :

The safety precautions mentioned by Hill and Knott are, in the opinion of the writer, completely misleading, particularly the statement at the top of p. 101 under the heading Conclusions " its burning effects, in liquid form, are more severe than most acids ". If ever there was an understatement, this is it. My own personal experience with this acid dates back to 1939 when in control of pilot plants producing 80% acid and, a year or so later, anhydrous hydrofluoric acid. This was before the days of the discovery of calcium gluconate as a material to be injected into a burn by a medical officer, which stops the intense pain immediately. The writer has actually seen men nearly mad with pain from a comparatively small burn and there is plenty of evidence medically of mutilated hands, with fingers lost due to the action of this acid, and yet the authors have the temerity to class this as merely "more severe than most acids ". Personally, having handled a very wide range of extremely dangerous chemicals, the writer still puts this particular acid in the highest place.

On p. 101 it states that it has been found possible to tolerate small leaks. That is a terrible admission for a chemical engineer to make! Anyone with plant experience knows how a trace of vapour can affect the face soon after shaving, involving the necessity to rub magnesia paste over the face to avoid the reddening and stinging resulting therefrom.

Another statement on p. 101 says " operators wear face shields and gloves in addition to normal overalls ", but on a plant of this sort it should be light protective kit at least when carrying out inspections or valve operation for the risk from the acid is there.

Eyeshields are also mentioned. This should of necessity be face shields and operators who use otherwise are asking for trouble.

Finally, on p. 95, it is stated that acid of over 60% strength will cause immediate apparent damage and pain. This is definitely not a true statement. It is entirely dependent on the type of skin in contact with the acid. Anhydrous hydrofluoric acid burns can remain undetected for hours. One further extreme understatement is " contact with the eyes is particularly dangerous and can cause blindness ". The only real treatment of an anhydrous hydrofluoric acid burn is injection of calcium gluconate, but this cannot be done with an eye. It is therefore absolutely essential that perfect eye protection must be worn at all times to ensure that at all costs no hydrofluoric acid can reach the eye. The situation is a far more serious one than the article would have us believe.

Mr. HILL wrote in reply to Dr. Burrage :

It was not intended that the present paper should state the medical problems of handling hydrogen fluoride other than briefly ; in view however of the comments of Dr. Burrage, Dr. F. W. Meichem of U.K.A.E.A. Springfields Works has contributed the note following this reply.

The toleration of small leaks is largely dependent on how small is small. Springfields' experience with hydrogen fluoride dates back to 1946 and with the small leaks that are tolerated we have not experienced or seen any possibility of the serious casualties of Dr. Burrage's experience. It is evident that the tolerated leaks described in the paper are orders of magnitude smaller than those envisaged by Dr. Burrage.

The experience in the use of protective clothing described on p. 101 can be amplified. Face shields or eye shields, gloves, and normal overalls are worn for normal operation in the reactor cells where the hydrogen fluoride is essentially gaseous ; in those cells containing hydrogen fluoride boilers and the distillation plant, light P.V.C. coveralls are worn in addition.

The choice of eyeshields rather than face shields on maintenance work is to some extent a matter of opinion. Eyeshields are preferred at Springfields as giving positive protection to the eyes whereas face shields although giving some facial protection give only partial protection to the eyes. Cases have occurred, not with hydrofluoric acid, where splashes have entered the face shield and injury has resulted.

Dr. MEICHEN's comments are given below :—

". . . It is clear that Dr. Burrage has been strongly influenced in his comments by unfortunate happenings in the pre-war period, which we have been able to avoid.

". . . I think it is fair to say that hydrogen fluoride is a particularly nasty substance—the more so in that the type of burn produced tends to progress for a much longer period and therefore damage is more widespread than with most of the other acids in common use in industry. However, we have had no serious mishaps at Springfields, and probably the twenty-odd years of progress in safety methods and plant design have played a major part in preventing this, and in addition there have been certain developments in technique of which Dr. Burrage is obviously unaware.

" Without in any way attempting to belittle the effects of this substance, I think that it is unwise to rush into the other extreme and credit it with destructive powers beyond those which it does possess. For example, it is not correct to give the impression that all hydrogen fluoride will produce burning, no matter how low the concentration. The example which he quotes of the skin smarting after shaving is a particular case : after shaving there are many tiny areas denuded of their protective material, and any strong acid, or even a particularly cold blast of wind, would produce a reactive effect locally. In the case of hydrogen fluoride, normal uninjured skin will tolerate 0·2% on contact for twenty-four hours without visible or irritant effect. Skin which does not do this would indicate a hypersensitivity. The results of a study of this and other acids can be found in Merewether.[3]

" With regard to actual treatment, we have for some years now forsaken the calcium gluconate therapy, which can be extremely painful in certain areas which are likely to be the site of an accident (*e.g.* the finger-tips, where tissue is somewhat scanty), and nowadays we tend to use the ice therapy, followed by treatment with one of the cortisones, which, of course, were not available in 1939 ; the results of treatment of this nature have been extremely good.

" I am in agreement with Dr. Burrage's very forcible point of view regarding eye protection : there is no doubt that the eyes are particularly vulnerable. This is the case not only with this acid but with any other, and damage to the fine tissues can easily result in scarring, with subsequent impairment of vision. In all chemical operations we do stress that it is vitally important to deal with any injury of this type at once, on the spot. What is done within the first fifteen seconds probably decides the issue, and this is why, throughout the plant at Springfields we keep a liberal supply of first-aid equipment for eyes."

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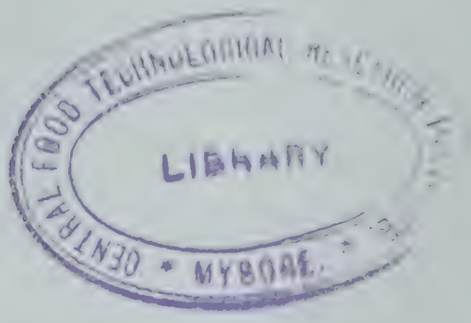

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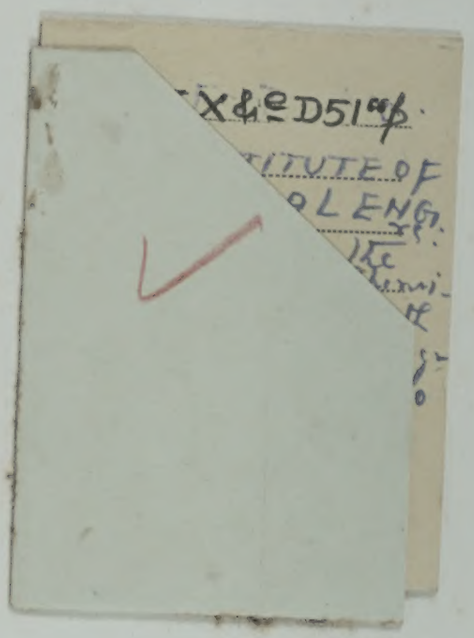
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